



**UNIVERSITY
OF OULU**

FACULTY OF TECHNOLOGY

**CELLULOSE-BASED ABSORBENTS FOR OIL
SPILL RESPONSE:
TESTING IN SIMULATED ARCTIC MARINE
CONDITIONS**

Okyere Abayie Samuel

ENVIRONMENTAL ENGINEERING

Master's thesis

May 2019



FACULTY OF TECHNOLOGY

**CELLULOSE-BASED ABSORBENTS FOR OIL
SPILL RESPONSE:
TESTING IN SIMULATED ARCTIC MARINE
CONDITIONS**

Okyere Abayie Samuel

Supervisors:

Prof., Docent, D.Sc. (Tech) Eva Pongrácz

Prof. Henrikki Liimatainen

Docent Ossi Laitinen

DI Victor Pavlov

ENVIRONMENTAL ENGINEERING

Master's thesis

May 2019

ABSTRACT

FOR THESIS

University of Oulu Faculty of Technology

Degree Programme (Master's Thesis)		Major Subject (Licentiate Thesis)	
Environmental Engineering		Water, Energy and Environmental Engineering	
Author		Thesis Supervisor	
Okyere Abayie Samuel		Pongrácz, E., Professor, D.Sc. (Tech) Liimatainen, H., Professor Laitinen, O., Docent Pavlov, V., DI.	
Title of Thesis			
Cellulose-based absorbents for oil spill response: Testing in simulated Arctic marine conditions			
Major Subject	Type of Thesis	Submission Date	Number of Pages
Water and Environmental Engineering	Master's Thesis	May 2019	81
<p>Abstract</p> <p>Due to the increased concern of risks of oil spills in the Arctic marine environment, the search for alternative, a sustainable oil spill response technology has intensified. Especially, development of cost-effective, reusable and environmentally friendly sorbents from renewable resources have gained significant interest. The objective of this thesis was to study bio-based sorbents obtained from nanocellulose materials, i.e. aerogels, and address their oil absorption capacity and performance under Arctic marine conditions. Laboratory conditions were designed to simulate the conditions of Oulu and Tromsø ports. In general, nanocellulose based aerogels display high mechanical strength, high surface area, are cost-effective and safe to handle compared to many synthetic materials.</p> <p>In this thesis, hydrophobized cellulose nanofibril aerogels produced from recycled fibre waste were used to absorb diesel and hydraulic oil. The nanofibrils were obtained using a simple and environmentally friendly nanofibrillation treatment after which aerogels were fabricated using freeze-drying process in the presence of two silylation agents. The Arctic weather conditions were simulated using a climate chamber. The weather conditions simulated were temperature, shaking and no-shaking frequency (to represent ocean waves), ice and no-ice condition and water salinity of 1% (Oulu port) and 3.5% (Tromsø port).</p> <p>The nanofibrillation and hydrophobic silylation of waste cellulose fibres resulted in nanofibrillar aerogels, which had an ultralow density (0.01 g/cm³) and high porosity (99.15%) after freeze-drying and heating. The cellulose nanofibril aerogels showed higher oil (diesel and hydraulic) absorption performance in both 1% and 3.5% salinity than the commercial material. The diesel oil absorption by the nanofibril aerogel was higher in 1% salinity while the hydraulic oil absorption was better in 3.5% salinity. In particular, the nanofibril aerogels had diesel oil absorption capacity of 59.9 g/g (1% salinity) and hydraulic oil absorption capacity of 43.4 g/g (3.5% salinity), which is much higher to those of commercial absorbent materials, i.e. polypropylene, with diesel oil absorption capacity of 15.6 g/g in 1% salinity and hydraulic oil absorption capacity of 12.4 g/g in 3.5% salinity.</p> <p>The shaking and icy conditions affected oil absorption with the nanofibril aerogels more than the commercial material. Overall, oil absorption was higher under shaking conditions compared to the no-shaking. The presence of ice decreased the absorption capacity of nanofibril aerogels and the commercial material. Generally, oil absorption capacity of the nanofibril aerogels was higher than that of the commercial material in all the conditions. The above advantages make nanofibril aerogels promising absorbents for removing oil spills from ports (Oulu and Tromsø).</p> <p>KEYWORDS: aerogels, oil spill response, Arctic, marine pollution, cellulose absorbents, nanocellulose, absorption</p>			

PREFACE

This thesis was done as part of APP4SEA project funded by Northern Periphery and Arctic (NPA) 2014-2020 programme. The study was done at the Water, Energy and Environmental Engineering Research Unit, University of Oulu, Finland.

The APP4SEA project seeks to strengthen the preparedness of environmental authorities and the awareness of the public (students, researchers, and professionals) in the coastal areas of the NPA region about oil spill response. The project aims to unite coastal authorities, pool their competencies and provide data on oil weathering, best response techniques and models available.

The study is intended to describe one of the fastest growing oil response tools, which is available for response to oil spill in the Arctic and the industry. This method is one of the environmentally friendly response tools currently. In the study, references are made to other useful documents relating to oil spill response including publications, reports and other conference materials of organizations involved in oil spill research and response technology.

I would like to praise the Almighty God for giving me the strength I needed to carry out this thesis. His love, support, and abundant grace have kept me through my educational career and my stay in Finland. My special thanks and profound gratitude go to Professor Prof. Eva Pongracz for her support, matchless love, encouragement and being a solid pillar in my entire academic work in the university. I am forever grateful for the leadership role; belief you had in me, and the opportunities you gave me through my student life. I am honoured to say that the knowledge you have impacted to me through the courses I had with you will be irreplaceable. I also thank Prof. Henrikki Liimatainen for his superior role in my current level of success. I could not have achieved a better result without your magnificent supervision, advice and special contribution. My appreciation again goes to Doc. Ossi Laitinen who has been the backbone and anchor of my laboratory work and Thesis analysis. Your effortless sense of lifestyle, professionalism, readiness, and understanding made me achieve this success. My special thanks again go to DI. Victor Pavlov for his invaluable support and assistance provided towards my work from the beginning to the end. This work could have not been completed without your great input, time and advice.

Other thanks to the members of the Energy and Environmental Engineering (EEE) research group for their love and friendly support they have shown me since my employment as a diploma worker. In addition, to the Fibre and Particle Research Unit who provided the laboratory for the experiments to be conducted. Special thanks to my office colleagues Antonio and Elena for keeping me company and active all the time in the office. I will also thank Mr. and Mrs. Dapaah and Dr. Koduah Dapaah for their kind support to my studies in Finland. Finally, yet importantly, my thanks go to the entire Okyere-Abayie, which include my siblings Matilda, Rejoice, Spafford, Esterline, Anita, Leticia and Ernest for their unconditional love.

This thesis is dedicated to my father Mr. Samuel Okyere Abayie and my late mum Mrs. Veronica Asantewaa Okyere Abayie for their superior authority and amazing love throughout my academic career.

Oulu, 22.5.2019

Okyere Abayie Samuel

TABLE OF CONTENTS

ABSTRACT.....	3
PREFACE	4
TABLE OF CONTENTS	6
ABBREVIATIONS AND DEFINITIONS	8
1 INTRODUCTION	9
1.1 Objectives of the study	12
1.2 Outline of the study	12
THEORETICAL PART	14
2 POLLUTION AT ARCTIC HARBOURS AND COASTAL AREAS: A CASE OF OIL SPILLS	15
2.1 Sources of marine contamination at harbours	15
2.2 Harbour conditions: cases of the Norwegian and Baltic Seas	17
3 EFFECTS OF ARCTIC MARINE CONDITIONS ON OIL SPILL RESPONSE..	20
3.1 Overview of Arctic marine conditions	20
3.2 Effect of ice on oil spill response	21
3.3 Oil types and their properties	22
3.4 Marine Arctic weathering of oil slicks	25
4 OIL SPILL RESPONSE TECHNOLOGIES: APPLICATION OF SORBENTS...	31
4.1 Overview of primary and secondary oil spill response technologies	31
4.2 Application of sorbents	31
4.2.1 Forms of absorbents	33
4.2.2 Characteristics of absorbents.....	33
4.2.3 Limitations of absorbents	34
4.3 Classification of absorbents.....	35
4.3.1 Absorbent materials	35
4.3.2 Cellulose-based materials.....	38
4.4 Aerogel as oil absorbents	40
4.4.1 Nanocellulose-based aerogels oil absorbents.....	41
4.4.2 Bacterial cellulose aerogels as absorbents	44
4.4.3 Carbon aerogels as absorbents	44
EXPERIMENTAL PART	45
5 MATERIALS AND METHODS.....	46
5.1 Materials	46
5.2 Fabrication of hydrophobic cellulose nanofiber aerogels	46

5.3	Sorption of oils using aerogels	48
5.4	Absorption capacities	51
5.4.1	Diesel oil absorption using CNF aerogels and commercial reference	51
5.4.2	Hydraulic oil absorption using CNF aerogels and commercial material ..	51
6	RESULTS AND DISCUSSION	52
6.1	Hydrophobicized cellulose nanofiber aerogels	52
6.2	Oil absorption	53
6.2.1	Low salinity (brackish) environment (10 ppt)	53
6.2.2	High saline environment (35 ppt)	55
6.2.3	Comparison of the behaviour of hydraulic and diesel oils in different salinity	56
6.2.4	Effect of hydrodynamic conditions.....	57
6.2.5	Effect of ice on oil absorption.....	60
6.2.6	Effect of temperature on oil absorption	62
6.3	Limitations of the study.....	63
6.4	Recommendations for further research	63
7	SUMMARY AND CONCLUSIONS	65
8	REFERENCES	67
	APPENDIX:.....	78
	APPENDIX 1. GLOSSARY	78

ABBREVIATIONS AND DEFINITIONS

BC	Bacterial Cellulose
CNC	Cellulose nanocrystals
CNF	Cellulose Nanofibril
CNT	Carbon Nanotube
HDTMS	Hexadecyltrimethoxysilane
MTMS	Methyltrimethoxysilene
NGO	Non-Governmental Organization
NO _x	Nitrogen Oxides
NS	No-Shaking
OSR	Oil Spill Response
RC	Regenerated cellulose
RGO	Reduced Graphene Oxide
SACs	Special Areas of Conservation
SH	Shaking
SO _x	Sulphur Oxides

1 INTRODUCTION

The world at its growing population consumes about 14 million m³ of oil per day or 162 m³ per second. In view of this, many oil companies are now exploiting new areas of oil and gas deposits and also considering Arctic as a potential unexploited oil and gas source. (Muizis 2013) Quick changes in climate is prominent to the evacuation and diminishing of Arctic ice and this gives access to increasing commercial activities in the Arctic **marine environment** (see Glossary) (Glickson et al. 2014). At the same time, oil spills have generally been recognised serious concerns by industries, non-governmental organisations (NGOs) and governments due to their impact on the environment and human health (Aljammal and Juzsakova 2016). Oil spill in the Arctic is a risk, presenting itself as hazard to Arctic nations and their neighbours (Glickson et al. 2014).

Oil spill is an accidental release of hydrocarbons into the marine environment, which forms a slick on the water surface, and has certain physical and chemical properties and can undergo several natural transformational processes: spreading, emulsification, dispersion, evaporation, dissolution, oxidation, biodegradation, and sedimentation. Oil spilled on water disperses on water, submerges and accumulates into the sediments by wind and currents. (Daling and Strøm 1999; Doshi et al. 2018)

It is important to note that ports and harbours are known to facilitate maritime transportation of essential goods and services; therefore, all ports and harbours in North America, Europe, Asia etc., are at risk of oil spill pollution (Hossain 2018). Oil spill remains a key **pollutant** from port activities. The causes of oil spills at the ports are from operations such as loading and bunkering, transport of oil in tankers, accidental or illegal discharges of tank washings and oil contaminated ballast water. Most of the oil discharges are done deliberately and this requires much attention. Over 80% of reported spills happen at ports but majority of them are small. These spills are not only a concern of ports with oil terminals and commercial traffic but also small ports and marinas can contribute to the amount of oil that enters the marine environment to cause pollution. (SACs 2001)

In the Arctic, oil spill response is difficult due to the challenging weather and the environmental condition. The information of many processes such as physical phenomena (**ice cover**, marine weather, and coastal processes) are significant to structure the environmental framework for the marine ecosystem (EPPR 2017). The Arctic is a polar region at the Northernmost part of Earth, of which the Baltic and the Norwegian

Seas are found in the European Union (EU) (Walday and Kroglund 2002). There are many shipping activities that takes place on the Baltic and Norwegian Sea, and the possibility of oil **pollution** due to these harbour activities are high (HELCOM 2018). Oulu port and Tromsø port are found along the Baltic and Norwegian sea (Port of Oulu 2019; Port of Tromsø 2019). The Baltic Sea alone transports over 160 million tons of oil every year (HELCOM 2018). When considering effective and safe oil spill response (OSR) strategy in the two ports, parameters such as air and water temperature, wind velocity and hours of daylight are very important to consider (EPPR 2017). The Arctic region is very vulnerable due to the slowness of biochemical processes and these have an effect on oil spill response. The water shows weak **mineralization** (50-200 mg/L) and mostly **neutralization reactions** of pH 7, which explains the poor ability of microbes to digest the hydrocarbons. Moreover, the cold weather slows oil evaporation. (Muizis 2013)

In the Baltic and Norwegian Sea, salinity of water differs contingently on depth and location which also affect the behavior of spilled oil. Water salinity at the port of Oulu is about 10 ppt while that of the Norwegian Sea is about 35 ppt. (Loeng and Drinkwater 2007; Lampela 2011). On the Baltic Sea where Oulu port exists, there is an ice cover, a water temperature of 0 °C in the winter and 16-19°C in the summer, and unevenness of wind fields, which have an effect on harbour activities (HELCOM 2018). On the other hand, on Norwegian Sea where Tromsø port exists, there is no ice cover and the water temperature is usually 0 °C in the winter (Loeng and Drinkwater 2007).

There are numerous countermeasures and OSR tools for the removal of oil in the Arctic. These methods include in situ burning, mechanical method, chemical methods, thermal methods, **bioremediation** and absorption method (Ortea et al. 2006; Lampela 2011; Ghaly and Dave 2011; Angelova et al. 2011; ART 2015). All these methods can be used either together or separately. Absorbents are usually used at the final stages of oil spill recovery and can be used for removal of small spill volumes. Nevertheless, absorbents can be cost-effective and environmentally friendly response method especially with the spills happening near coastal areas. (Sabir 2015; Aljammal and Juzsakova 2016).

Absorbent materials are grouped into classes such as synthetic polymer sorbents, natural organic absorbents, and inorganic absorbents. The synthetic sorbents include polypropylene materials, the inorganic sorbents are made of fine-grained and natural inorganic material, while the natural based absorbents are made up of plant residues such as sugarcane bagasse, rice straw, cotton etc. (Ghaly and Dave 2011; Sabir 2015; Aljammal and Juzsakova 2016). The synthetic materials are mostly used commercial

absorbents for oil spill clean-up. They have a disadvantage of disintegrating slowly compared with the natural absorbents. (Teas et al. 2001) In contrast, natural absorbents are more environmentally friendly OSR alternatives. Other benefits include their **recyclability**, high oil recovery capacity (usually 3-50 times their own weight), smaller density than that of inorganic and synthetic absorbents, easy disposal and outstanding biodegradability. (Annunciado et al. 2005; Wahi et al. 2013; Laitinen et al. 2017) Notwithstanding these advantages, a lot of natural sorbents have disadvantages of poor **buoyancy**, poor oil selectivity as a result of water uptake of these characteristically hydrophilic materials (Laitinen et al. 2017). To successfully collect oil spills from water, the absorbents should have a high sorption capacity, **porosity**, excellent oil-water selectivity, and a quick oil sorption rate. Furthermore, the material would be beneficial if the absorbent is low cost, recyclable and produces less secondary pollution. (Wahi et al. 2013)

Recently, there have been several types of research into cellulose nanofibril aerogels, which are natural sorbent materials for oil removal. These **porous** and ultralow density cellulose aerogels are built on cellulose nanofibrils (CNFs) with good mechanical characteristics, low density, environmentally friendly, natural biodegradability, high porosity and renewability, which makes them potential to be used as oil absorbents. (Korhonen et al. 2011; Cervin et al. 2012; Zhang et al. 2014; Mulyadi et al. 2016; Zhou et al. 2016; Zanini et al. 2017; Liu et al. 2017) CNF aerogels contain abundant hydroxyl groups that make them display amphiphilicity, i.e. they have a poor inherent performance of absorbing oil and **hydrophobic** compounds and there is the need to enhance the hydrophobicity of these aerogels to have good affinity towards oils (Sai et al. 2013; Jiang and Hsieh 2014; Wang et al. 2014).

The aim of this study was to address shoreline oil spill clean-up. A comparative analysis was performed under simulated Tromsø port (Norwegian sea) and Oulu port (Baltic sea) environmental conditions (ice-infested, no-ice, saline water (1 and 3.5%), cold weather and waves). In this study, hydrophobized CNF aerogels were used for the clean-up in a simulated Arctic marine condition in the laboratory. The simple but environmentally friendly nanofibrillation treatment, followed by freeze-drying combined with two silylation treatments were used for the fabrication of the hydrophobic CNF aerogels. To the best of knowledge, this was the first time when a silylated and nanostructured aerogel have been used to remove oil (diesel and hydraulic) in a simulated Arctic condition. The prepared CNF aerogel exhibited ultrahigh oil (diesel and hydraulic) absorption capacity

under both 1 and 3.5% salinity which was notably better than that of a commercial material (polypropylene). Interestingly, the diesel oil absorption capacity was higher in 1% salinity while hydraulic oil absorption was higher in 3.5% with the CNF aerogel.

1.1 Objectives of the study

The objectives of this study were:

- Organising an installation in the laboratory, which simulates winter environmental (sea and ambient) conditions of the Arctic sea harbour.
- Study bio-based sorbents obtained from nanocellulose materials, i.e. aerogels, and address their oil absorption capacity and performance under Arctic marine conditions.
- Compare the performance of CNF aerogels to existing commercial absorbents.

1.2 Outline of the study

The thesis outline is structured in three (3) steps as shown in Figure 1, by first working with the literature review of the study (theoretical background) and building background studies before the experiments. The theory includes oil pollutions at Arctic harbours, the effect of Arctic marine conditions to oil spill and response technologies. This is followed by the experimental part which consist of materials and methodology (fabrication of CNF aerogels and experimental setup), results and discussion (prepared CNF aerogel, oil absorption rates, study limitations and recommendation for future studies), and finally a conclusion.

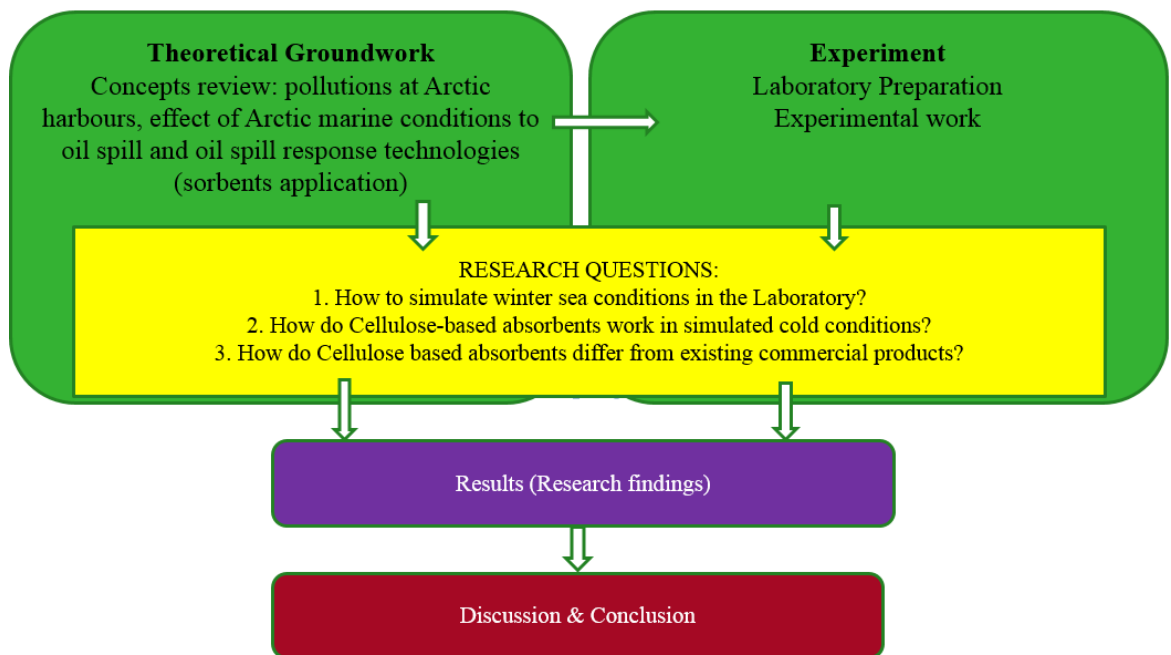


Figure 1. Outline of thesis

THEORETICAL PART




2 POLLUTION AT ARCTIC HARBOURS AND COASTAL AREAS: A CASE OF OIL SPILLS

2.1 Sources of marine contamination at harbours

Harbours (ports) serve as channels for international trade by the accommodation of liner shipping and cruising. Ports are known for activities such as loading and unloading cargoes, storage of goods, warehousing, packaging and accessing of inland transportation. (Hossain, 2018; Pettit and Beresford 2009) With regards to the environment, ports can be associated with a number of effects: **emissions** due to port activities and operations, **maritime traffic**, and intermodal traffic linking the port vicinity (Lam and Notteboom 2014). Table 1 shows some of the key pollutant sources at the Arctic harbours. Contamination sources such as greenhouse gases (NO_x, SO_x and CO₂) emission are obtained from ship operations and energy use, **ballast water** discharge when the ship is unloaded or loaded, sewage disposal from toilets, urinal, and WC scuppers, and dust originate from cargo operations and, **hazardous cargo** is also obtained from dangerous materials covered by IMDG (International Maritime Dangerous Goods) code. (OECD 2011; Lam and Notteboom 2014; Hossain 2018). In this study, the main focus will be on oil spills and their impact on the marine environment.

Table 1 Sources of contaminants at the harbours (adapted from Hossain 2018)

Contaminant sources	Within the Port area	At Sea	Shore land areas
Exhaust (NO _x and SO _x)			
CO ₂ emissions			
Ballast water handling			
Oil spill			
Sewage disposal			
Dust			
Handling of hazardous cargo			

 = severe
 = Medium impact
 = None

There are many ways that oil can enter the marine environment. These include oil spills from natural seeps from the bottom of the ocean and anthropogenic sources including leaks and human activities such as accidental incidents, operational incidents and illegal discharges from shipping activities as well as tanker accidents leading to a large oil spill (HELCOM 2009; OECD 2011; HELCOM 2018). Over 80% of oil spill incidents occur within ports and harbour areas but most of the spills are small and are due to normal operations such as loading and unloading, discharging and bunkering. Moreover, many small spills are difficult to observe and regulate. Other contributions ensue from the transportation of oil in tankers, which includes illegal discharges of tank washings and oil-contaminated ballast waters. Nevertheless, the problem of oil pollution is not only a worry for harbours with oil terminal or related commercial activities but rather small harbours also contribute to the marine oil pollution. (Suchanek 1993; SACs 2001; HELCOM 2018)

Contamination of the marine environment at the harbour affects the invertebrate population and the species that form the marine ecosystem. They are subjected to stress from both severe and chronic oil toxicity and it results in mortalities. (Suchanek 1993) A Report by HELCOM (2018) shows that a small amount of oil on the sea can contaminate the plumage of waterbirds by reducing their buoyancy and thermal insulation. In this same report, oil spills were monitored by focusing on the busiest shipping routes using aerial surveillance in the core indicator (Operational oil spill from ships) evaluation. The results show that the operational oil spills from ships were below threshold value on most of the Baltic Sea area. Figure 2 shows a decline in oil spillage in the Baltic Sea though there is increase in shipping activities. This finding suggests that measures taken to reduce oil spills have been successful.

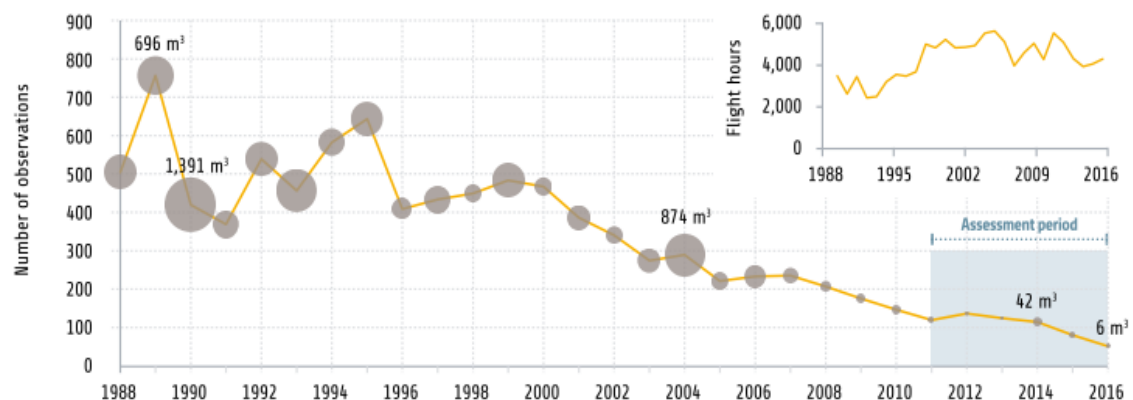


Figure 2. Oil spill detection by Baltic Sea countries between 1988 and 2016. The size of the circles specifies the amount of spilled oil in cubic meters. On the y-axis is the number of observed illegal oil spills. (HELCOM 2018)

2.2 Harbour conditions: cases of the Norwegian and Baltic Seas

The Arctic Ocean is divided into different regions. In this study, focus is on the EU part of the Arctic Ocean where Norwegian and Baltic Sea are located. The European part of the ocean as shown in Figure 3 is about 8% of the total area of the Arctic Ocean and this is about 25% of the total volume of the ocean due to the depth. (Walday and Kroglund 2002) The area of the ocean exists between the Scandinavia, Greenland, Novaya Zemlya and the North Pole, Baltic Sea, Norwegian Sea, Icelandic Sea, and the Greenland Sea. According to statistics, the surface area of the European part of the Sea is about surface temperature varies around -1.6 -14°C and its salinity is about 30-35.4%. (OSPAR 2000; Walday and Kroglund 2002; Word 2014)

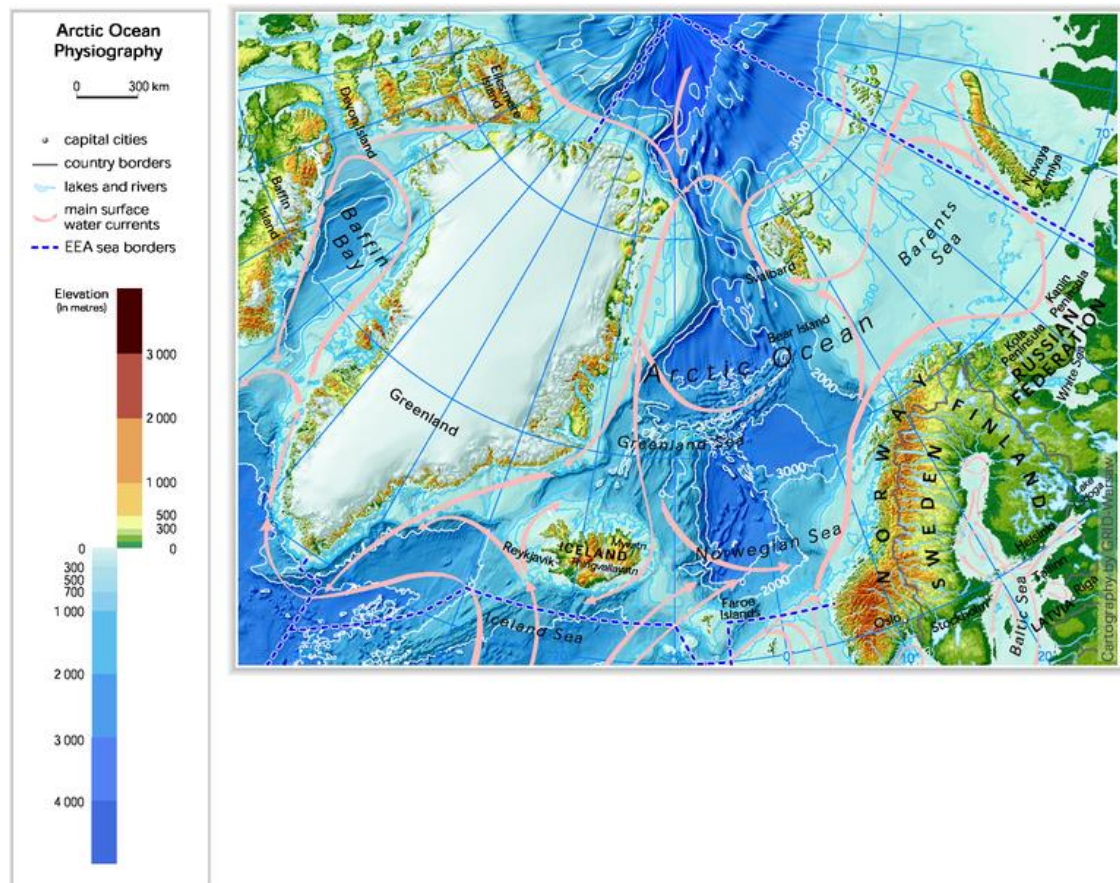


Figure 3. Arctic Ocean physiography (depth distribution and main currents, seas and rivers in the European part) (EEA 2009).

The Baltic Sea is considered as one of the largest water areas in the world, which contains more salt compared to freshwater but not like seawater and it is located between the continental and maritime climate in a transition zone (Meier 2006; HELCOM 2018). The Baltic Sea has a drainage area 4 times larger than its surface area, which is about 420 000 km² and one-third of the sea is shallower than 30 meters. Every winter, there is an inflow

of marine water in the Baltic Sea during the winter storms. The water inflow has a higher salinity and it also increases oxygen content in the water. (HELCOM 2018) The Northern part of the Baltic Sea is the Bothnian Bay, which is typically **brackish water**. On the coast of the Bothnian Bay is where Port of Oulu is located, and it remains the largest Port on the Bothnian Bay. The Port of Oulu is also a home for a larger number of species (Port of Oulu 2019). The salinity of the water is different at various depths of the sea and this is because water density increases with salinity. The sea exists in a **temperate climate zone** and in the northern part of the sea; it has longer winter consisting of stronger frost, whilst the southern part has moist and mild winters. The degree of ice cover has decreased in the Baltic Sea in recent years, which is illustrated in Figure 4. In the winter, the temperature of the water is about 0°C and 16-19°C in the summer. (HELCOM 2018)

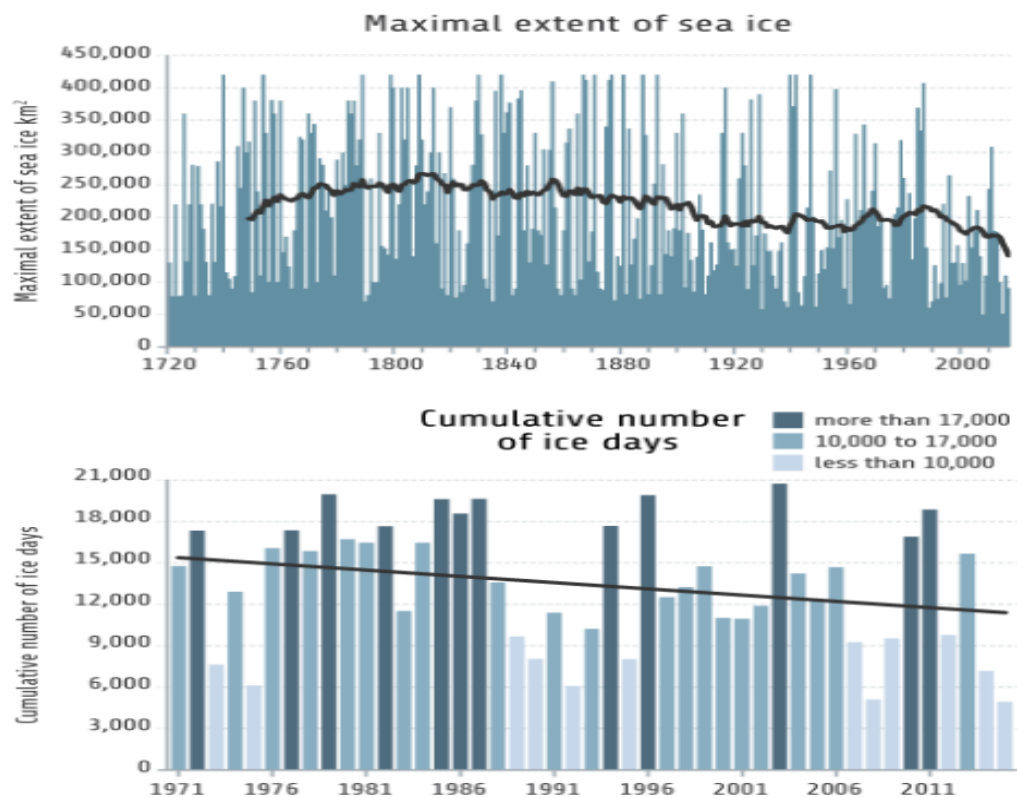


Figure 4. Development of ice cover in the Baltic Sea. The graph above represents the maximum degree of sea ice in the winter for over 300 years, whilst the black line gives 30 years average. The lower part of the graph indicates cumulatively number of ice days per winter (HELCOM 2018)

The Baltic Sea has a high unevenness of wind fields at various sub-basins, complex depth profile and ice cover, which affects the behaviour of waves on the sea. The waves have a significant effect on coastal and offshore activities such as harbour operations, shipping, offshore platforms, human safety, and coastal infrastructure. The wave variations on the

Baltic Sea is strongly due to anthropogenic climate change. (Groll et al. 2017) 160 million tons of oil is transported in the Baltic Sea every year. The sea contains several species and areas such as fish spawning and feeding, birds, and mammals rest areas. (HELCOM 2018) Furthermore, Baltic Sea has a salinity of 10‰ of average ocean water salinity, low mean temperature and ice cover all over the northern Baltic Sea annually. The ice in the Baltic Sea is solid because of low salinity and there are no brine channels. In this case, oil sticks on the ice block weakly making easier to remove with lower energy. Low water salinity in Baltic may sometimes cause heavier oils to sink, and this effect makes response procedures difficult. In the Baltic Sea, temperature can be -20 to -30 °C during the winter and in the winter; there is darkness, which makes oil spill response challenging. (Lampela 2011)

Other sea of interest in this study is the Norwegian Sea. **Topographically**, the Norwegian Sea occupies an area of 1.1 million km² with a volume exceeding 2 million km³ and has an average depth of 1 800-2 000 m. The sea has two separate basins (Norwegian and Lofoten basin), both with 3 000 to 4 000 m depth and a maximum depth 4 020 m and a salinity of 35 ppt. Furthermore, it has a levelled sea bottom with 100 m and 400 m depth and represents 49% volume of the Nordic Seas. (OSPAR 2000; Loeng and Drinkwater 2007; ICES 2008) Sand and clay deposits occupy the bottom substratum on the shelf but clay is usually found in the deeper section of the Sea (ICES 2008). Along the Norwegian Sea is the Tromsø Port. The port is the largest transport hub in Arctic Norway and a preferred port for fishing in Arctic waters (Port of Tromsø 2019). The Norwegian Sea is a changeover region for warm and saline water from the Atlantic to the Arctic Ocean (Blindheim 2004 as quoted in Torgersen and Huse 2005). The Norwegian is usually warm and has a salinity of 35 ppt. In addition, its circulation patterns and hydrographic conditions are affected by large-scale atmospheric patterns, which are reflected by North Atlantic Oscillation. (Hurrell 1995) There is no ice cover in the Norwegian Sea and this is due to the presence of warmth of the Atlantic waters and its ecosystem structure is affected by topography (Loeng and Drinkwater 2007).

In this study, experiments are conducted using the marine conditions of Oulu Port and Tromsø Port, which are located along both Baltic and Norwegian Seas. Experiments will be done to determine how oil spill removal by cellulose nanofibril absorbents is affected by both sea conditions.

3 EFFECTS OF ARCTIC MARINE CONDITIONS ON OIL SPILL RESPONSE

3.1 Overview of Arctic marine conditions

The Arctic Ocean covers a very large area under a very challenging condition with high seasonal and geographical variations in light, temperature and ice cover. The Arctic Ocean interchanges between cold and warm stages and the period of length of the states may vary. (Walday and Kroglund 2002) The temperature difference between summer and winter is small and the ocean is always at freezing point throughout the year (Word 2014; HELCOM 2018). When ocean mixing occurs, water temperature is higher than 0°C within the year round. For example, in some parts of the Arctic Ocean (Kara and the East Siberian Sea), water salinity is less than 20 ppt within the year and drops to 10 ppt during the summer. For the Arctic Ocean, salinity profile is the most significant perpetual stratification feature. (Word 2014)

However, changes in velocity and surface wind stress in the ocean replicates large scale of atmospheric pressure fields and characteristics of sea-ice concentration energy. The Arctic Ocean is also dominated by sandy and soft bottom substrate (fine grains, mud, clay, and sand) in its outer shelves and deep basins whiles gravel and courser remain predominant substrate on the shore areas and inner shelf. There are also harder substrates and rocky areas, which are notably important but are less common. (Word 2014) A portion of the Arctic is covered with ice year-round and its adjoining waters are covered with ice seasonally with changeable open water with the daylight of 24 hours (Lampela 2011; Word 2014; HELCOM 2018). During the summer, an area of 4 to 7 million km² in the northern part of the Arctic is covered with ice and about 14 to 15 million km² is covered in the winter. In the Arctic, snow melting changes the temperature and salinity of shoreline areas. (Word 2014) However, such nature of the Arctic environment makes spill response difficult and create problems for responders (Lampela 2011; Muizis 2013). This section discusses some of the conditions, challenges, and effects of Arctic conditions to response technique.

In the winter, OSR becomes difficult in icy conditions. The sea is covered by ice and the temperature in the Baltic Sea can sometimes be recorded as -20 and -30 °C. This usually affects response operations, methods, and equipment used for recovery. Conditions such as darkness in the winter and remoteness also have an effect on response operations. **Oil**

viscosity is increasing due to coldness, therefore, oils which had low viscosity and can be easily collected at high temperatures, becomes challenging, thereby making it problematic to be collected. The chilly weather is also making oils sticky, and contributes to the formation of oil lumps. (Lampela 2011; Muizis 2013) Consequently, there is also potential gelling of some crude oil types which have their pour points at 0 °C or below (Dickins 2017). Furthermore, winter conditions also have effects on oils buoyancy, and some oils loose their buoyancy especially in brackish water, with is low-salinity. In some cases, drifting ice put pressure on response tools and they may need to withstand ice pressure (Lampela 2011; Scholz et al. 2012). Under ice condition, cold temperature and reduction in wave energies will cause the oil to weather slowly and this extends the period of action for some types of countermeasures. In addition, when the ambient temperature reaches pour point, oil ceases from spreading and occupy less area. (Buist et al. 2008; Lampela 2011; Dickins 2017)

3.2 Effect of ice on oil spill response

Oil spill response (OSR) in the Arctic can be challenging, but also have potential positive factors in OSR operations (Dickins 2017). The Arctic conditions add extra environmental and logistical challenge but, in some cases, work to the advantage of responders. Firstly, the most apparent challenge is the presence of ice. Ice in its various forms can make it difficult to detect oil spill, encounter, contain and recovery of oil slicks with booms, skimmers, absorbents and other forms of vessel-oriented activities. Ice can also sometimes serve as a natural inhibition, preventing oil from spreading. On other hand, if the oil transports under the ice and are trapped on the blocks, OSR becomes more problematic. Oil under ice slows weathering and reduces waves. Evaporation, dissolution, and biodegradation are also very low in icy condition. Whereas the ice provides natural containment that offers an important advantage, oil slicks spread and drift fast in open water to cause impact before the introduction of response but in icy condition, the ice can contain the oil spills and offer time to mount for response. (Dickins et al. 2008; Lampela 2011; Scholz et al. 2012; Muizis 2013; Dickins 2017) More about the weathering process of oils is discussed in Section 3.4 in this study. Figure 5 shows fate and behaviour of oil in icy conditions. The natural variation of first-year ice thickness in combination with deformation features such as ridging and rubble offer naturally made pools, which contain the spilled oil beneath the ice cover inside a small area.

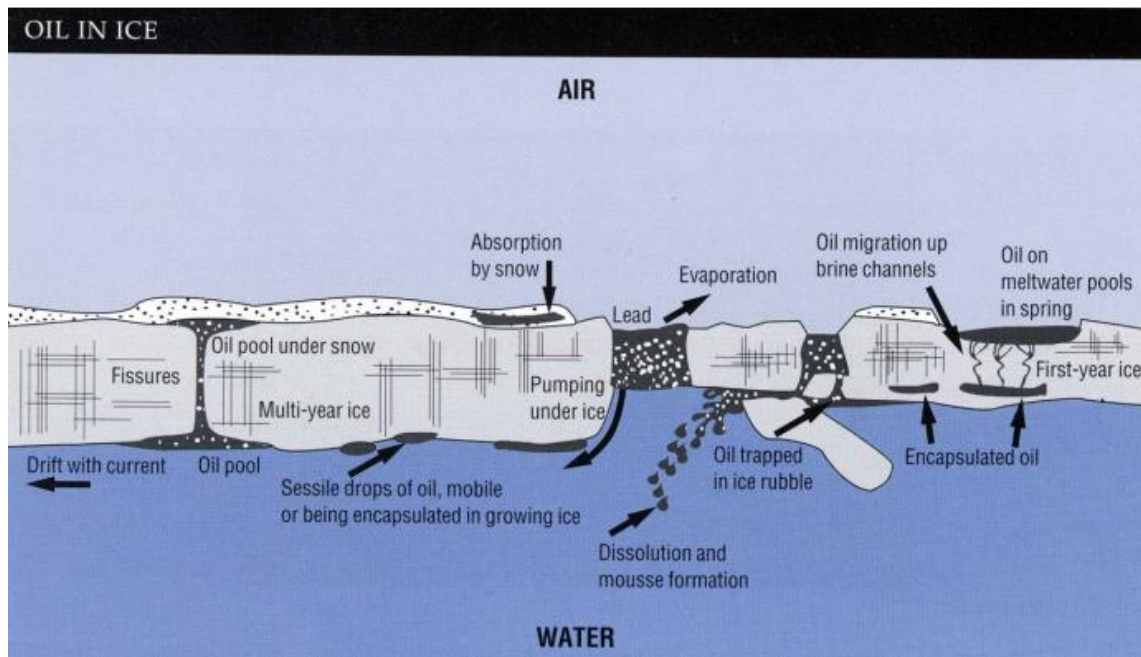


Figure 5. Fate and behaviour of oil spilled in ice ‘Oil and ice interaction’ (Bobra and Fingas 1986)

Oil spilled on ice or under the sea ice does not move alone but move along with ice drift. An experiment conducted by Buist et al. (2008) shows that oil required a current of 5 cm/s to move along under-surface of ice with smooth fresh ice to 15-30 cm/s under sea ice condition. Winter under-ice currents are not enough to transfer spilled oil from its original contact point together with ice undersurface. In **fiord zones** or in front of main deltas (Colville, Lena rivers and Mackenzie) where tidal currents are very stronger, currents are stronger to move oil but under-ice roughness can even restrict movement even in such a situation (Scholz et al. 2012). In addition, an oil spill in open drift ice moves in a different direction and at a different rate and this comes as a result of wind and currents (Buist et al. 2008).

3.3 Oil types and their properties

Marine oil spills consist of refined petroleum products (gasoline, diesel, etc.), heavier fuels (bunker fuels), crude oil, hydraulic oil and other waste oils (Ghaly and Dave 2011). The severity of the effects of oil spills is dependent on the magnitude of the oil and its properties (Holakoo 2001). Physical and chemical properties of oils have effects on the weathering processes. They lead to the transformation of oil states, .i.e., will make it difficult to recover the oil. (Daling and Strøm 1999) Oil is a complex mixture of **hydrocarbons** of different chemicals composition (e.g. toluene, benzene, naphthalene, methane, etc.). It is a **flammable liquid** with a specific smell and colour, which is extracted underground from sedimentary rocks. Oil is unable to dissolve in water but

soluble in alcohol and ethers. Generally, oils have a series of ranging viscosities with colour variations usually black and yellow and this is dependent on the composition of hydrocarbons. Oils are typically used as an energy source and a raw material for the chemical industry. (Muizis 2013) There are many compounds with different composition and properties present in oils and that makes them a very hazardous and problematic contaminant.

Chemical characteristics of an oil comprise of **molecular weight**, **melting point**, **partition coefficient**, **solubility**, **flammability limits** and **explosively limit**. The chemical properties vary depending on the type of oil. (ATSDR 1995; Ghaly and Dave 2011) Furthermore, the chemical composition of oil is dominated by hydrocarbons and it may include nitrogen, sulphur, oxygen and some metals (Olah and Molnár 2003, p. 45; Ghaly and Dave 2011). In addition, hydrocarbons have been categorised by the IUPAC by nomenclature. Nevertheless, crude oils are estimated to have 200-300 different compounds and out of that, 50-90% of the composition is hydrocarbons. They include

- Alkanes, which have low toxicity, **biodegradable** and exist in oil as gas form, liquids, and solids. They are the smallest form of hydrocarbons, which consist of saturated carbon and hydrogen atoms.
- Cycloalkanes are of carbon-hydrogen structures that form a ring, have 6 carbon atoms in a ring structure, and are poor biodegradable; yet very stable.
- Aromatic hydrocarbons containing an aromatic ring structure. (Manning and Thompson 1995, p. 8; Ghaly and Dave 2011)

There are four groups of fossil oils and they have different compounds such as saturated, unsaturated, aromatic and polar compounds. Averagely, crude oil has a composition of 30% paraffin or alkanes, 50% naphthenes or cycloalkanes. Aromatic compounds are volatile compounds (benzene, toluene, and xylene), bicyclic compounds (naphthalene), tricyclic compounds (anthracene, phenanthrene) and polycyclic compounds (pyrene) and they have 15% composition in crude oil. In addition, oils contains typical 5% of nitrogen, sulphur, and oxygen. (Manning and Thompson 1995, p. 9) Oil may also contain nickel and vanadium (Muizis 2013).

The behaviour of oil released into marine environment is not only affected by chemical composition but also by physical properties as well. The important physical characteristics of oil comprise of specific gravity, density, viscosity, flash point, colour, **surface tension**, and adhesion. The colour (dark brown or black) of oil can change

from yellow and green to red. (Holakoo 2001) The densities of crude oil mostly range from 0.70-0.99 g/ cm³ while that of seawater is 1.03g/ cm³. Therefore, the oil will float on seawater. Evaporation of lighter oil substances increases the specific gravity of oil, which may cause heavier oil fractions to sink and to form tar balls that may be able to interact with rocks and heavy sediments at the bottom of the water. (NASEM 2016)

The capability of an oil spill to spread quickly on the marine environment depends on its surface tension, viscosity, and specific gravity. The lower the surface tension of the oil, the higher is the rate of oil spreading, even in the absence of wind or currents. The surface tension of oils has a relation with temperature, thus the warmer the water, the faster the spread of oil, whereas the colder the water, the spreading is slower. (Ghaly and Dave 2011)

The viscosity of oils is determined by its large content of polar molecules (resin and asphaltenes), therefore the lower the components such as solutes and polar molecules the lower the viscosity. Oils with higher viscosity have a lower tendency of spreading out. (Ghaly and Dave 2011; NASEM 2016) In addition, temperature also influences on oil viscosity. The lower the temperature, the higher the viscosity of oil and this makes oil variations with temperature quite large. (NASEM 2016) When the temperature is increased from 10 to 50 °C, oil density reduces from 0.880 to 0.855 kg dm³ and viscosity from 5 000 to 200 cSt and this reduces oil resistance to flow (Nordvik et al. 1996). In addition, consequences in evaporation increase the viscosity of oils (See Table 2 for oil viscosity after weathering)

Table 2. Comparison of viscosity of crude oils after weathering (adapted from Fingas 2015, p. 559)

Type of Crude oil	Viscosity Before Oil Release	Viscosity After Initial Weathering (mPa-s)	Mass percentage (%) loss in weathering	Viscosity After Additional Weathering (mPa-s)	Mass percentage (%) loss in weathering
Light (Scotia light)	1	2	25	5	64
Medium (West Texas Intermediate)	9	16	10	112	35
Heavy (Sockeye Sour)	820	8,700	10	475	19
Diluted Bitumen (Cold Lake Blend)	270	6,300	15	50,000	30
Bitumen	260,000	300,000	1	400,000	2

Although adhesion or “stickiness” is a property that is not measured during industrial standard analysis. It has been noted as a problem at several spills. The stickiness of oil on surfaces can greatly impede clean-up of oil. (Jokuty et al. 1995; NASEM 2016) Another property, thus flash point relates to the temperature at which liquid or oil produces vapours for ignition by flame. Flashpoints for oils are wide-ranging whiles most fluids are flammable if their flash point is less than 60°C. Several fresh oils have many volatiles components and are flammable for a long period after spillage. This will depend on how highly volatile components will disappear by evaporation. Heavy oils are not flammable. (NASEM 2016)

3.4 Marine Arctic weathering of oil slicks

As soon as oil gets into contact with the marine environment, it becomes subject to several natural processes and these processes changes oil character and influence oil spill response operations (NRC 2003; Sørstrøm et al. 2010; Dickins 2017). Weathering depends on physical and chemical properties of oil, the amount of oil spilled, the surface area of oil exposed, wave, current, ice, weather and the location of the oil on either the

water or underwater (NRC 2003; ITOPF 2011; Scholz et al. 2012; Mapelli et al. 2017). Weathering processes in the Arctic include spreading and movement, evaporation, oxidation, dispersion, biodegradation, emulsification, dissolution and photo-oxidation (NRC 2003; ITOPF 2011; Scholz et al. 2012).

Spreading process is the horizontal expansion of oil spilled on water due to the force of gravity, inertia, surface tension and viscosity. Spreading is a significant process in the initial stages of oil spilled on Arctic water. Spreading increases the surface area of an oil slick and enhances mass transfer through evaporation and dissolution. (Njobuenwu and Abowei 2008) Oil begins to spread when oil is spilled and the rate of speed it takes to spread is dependent on the volume spilled and viscosity, which also depends on the composition of oil and temperature. For the oil to spread more quickly, the oil must have a low viscosity. A high oil viscosity will make the oil-spreading period longer and this is the case for the Arctic environment. Oil spills in the Arctic tends to have high viscosity due to low temperatures and this is because viscosity is inversely proportional to temperature. During the early spreading process, oils spread as coherent slick, nonetheless, they begin to break up rapidly. (NRC 2003; ITOPF 2011) Spreading is different in both ice and open water conditions. In the Arctic, the spread of oil is reduced by water temperature, snow, and ice, while the resulting oil slicks are much thicker than open waters. Usually, an oil can spread as ice begins to melt in late winter but is encapsulated and prevented from spreading when ice solidifies in the early winter. Figure 6 shows oils change in colour from black or dark brown to iridescent and silver sheen at the slick edge as they spread and reduce in thickness. (Board et al. 2014)

However, in open water, the pattern at which the wind blows affect the oil and it forms narrow bands, which is parallel to the direction of the wind. Therefore, the properties of oil become less significant when determining slick movement. Turbulence, waves, tidal streams and currents affect the spread of oil. When the combination of the forces is very low, the faster the spreading process. (ITOPF 2011; Dickins 2017)

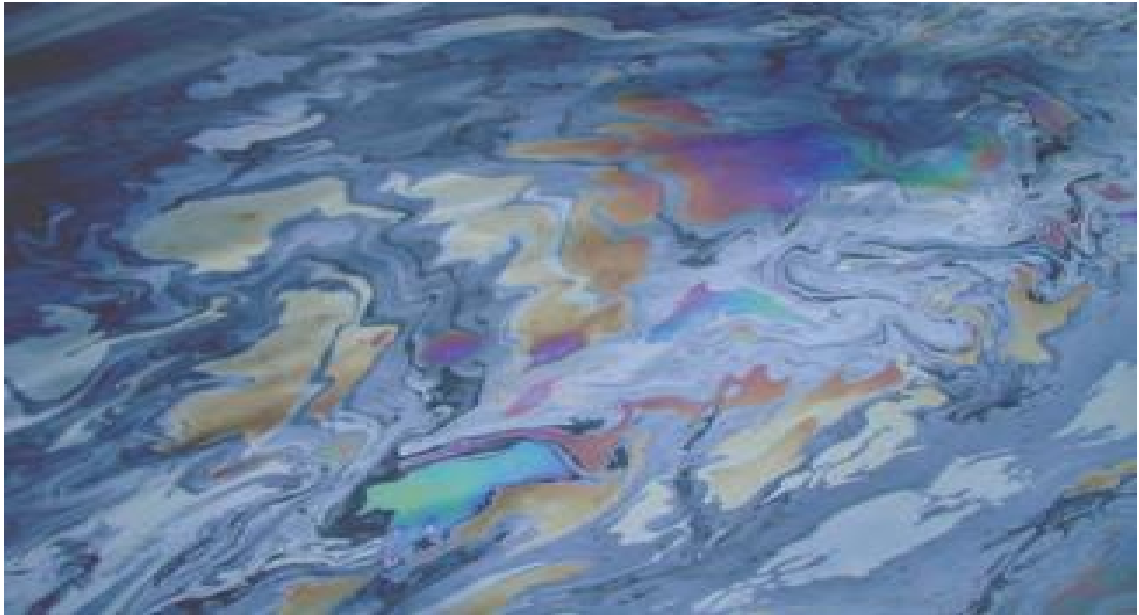


Figure 6. Thin films formed on medium and light oil as it spread in an appearance of a rainbow and silver sheen (adapted from ITOPF 2011)

Evaporation process is the transfer of light and medium weight oil components to vapour (Scholz et al. 2012). The process is very important in oil spillage, especially considering mass balance (NRC 2003). The evaporation rate is dependent on temperatures and wind speed. The lower the boiling point of the oil, the higher is its evaporation. For example, oil components with 200°C boiling point evaporate early (24 hours) under temperate condition (above -3°C but below 18°C). (ITOPF 2011) Evaporation of spilled oil is more slowly in sub-freezing temperatures and snow-covered spills. This is a special case for the Arctic environment. Several experiments have confirmed that oil spilled in packed ice will evaporate slowly compared to spills on open waters. This is primarily due to the oil thickness in pack ice. Furthermore, when oils are encapsulated in an ice sheet, they do not evaporate during the months of winter. Evaporation is slow under the Arctic environment due to cold water and low temperatures. (Scholz et al. 2012) The larger the surface area of oil (spreading) the faster lighter oil components will evaporate. Rough sea and warm temperatures also have an increasing effect on evaporation. According to research, refined kerosene and gasoline evaporate wholly in a short period, whereas light crudes loose over 50-75% of its original volume and medium oils loose about 40% of volume. In contrast, heavy oils tend to loose less than 10% of volume on its first day of the spill. (NRC 2003; ITOPF 2011)

Emulsification process is the process where water droplets are mixed with the spilled oil. This process forms highly viscous mixtures that have slow weathering tendency and are difficult to be burned, dispersed and physically recover (Scholz et al. 2012). Spilled oil in the sea takes up water and form water-in- oil emulsions, often called “chocolate mousse” (NRC 2003; Scholz et al. 2012). Emulsions form most readily for oils which, when spilled, have a combined Nickel/ Vanadium concentration greater than 15 ppm or 0.5% of asphaltenes content. These compounds and the state of the sea (wind speed of 3-5 ms⁻¹) defines the rate of emulsions formation. (Fingas et al. 2001; ITOPF 2011) The mixing of oil and water is driven by waves and wind (Scholz et al. 2012). Since emulsification is driven by wind-wave action, weathering processes are less dominant in ice condition, except under a condition where moving ice floes add surface turbulence. The wind-wave action is restrained by the ice availability thereby affecting emulsification. (Scholz et al. 2012) Therefore, emulsification is less dominant and slower process in the Arctic marine environment. Oils with high viscosity have slower emulsification than more fluid oils. Other compounds such as asphaltenes are able to precipitate from the oil and coat droplet of water, thereby increasing the stability of emulsions. The density of emulsion is almost close to that of seawater as the addition of water increases. However, steady emulations contain about 70-80% of water and are often semi-solid, and they are highly persistent and will remain emulsified definitely. Unbalanced emulsions may separate into water and oil when they are heated by sunlight under calm sea condition. (ITOPF 2011)

Dispersion process is the process where breaking waves forces oil droplets into the **water column** and this can make portions of the droplet small enough to persist in the water surface (Scholz et al. 2012). The dispersion rate is mainly reliant on the nature of oil and the state of the sea, mostly happening quickly with low viscous oil in the midst of waves action (ITOPF 2011). Dispersion in the Arctic marine environment is unlikely to happen in the freeze-up ice condition. Larger ice floes temporarily disperse oil into water columns around their edges and in most cases, larger oil droplets formed becomes too large to be dispersed permanently. This will then rise up to be deposited under the ice flows, therefore, oil dispersion becomes unlikely to happen in an Arctic environment. (Scholz et al. 2012) Waves and turbulence cause almost all the slick breaking into droplets with different sizes and mixes with the upper layer of the water column. The increase in surface area of oil enhances dispersion, whereas, the application of dispersant speeds up natural processes. (ITOPF 2011; Scholz et al. 2012)

Dissolution process is the process by which soluble water compounds in a surface oil slick dissolve into water columns below (Scholz et al. 2012). Oil spilled dissolution depends on the composition of the oil, spreading process, temperature of the water, turbulence and the extent of dispersion (ITOPF 2011). In the Arctic environment, the water is colder and icy conditions are dominant, however, dissolution rates are lower in cold climate regions than warmer ones (Scholz et al. 2012). For example, when oil is captured by ice, quite a small portion of the water-soluble components of the oil diffuses down to the bottom of the ice sheet, but at the bottom of the ice, concentration is very low (Faksness et al. 2011). Since oil spreading and dispersion is hindered by ice, low water temperature, and other Arctic conditions, dissolution will be affected as well. Chemical stabilization oil components in water are dependent on dissolution (NRC 2003). However, heavy crude components are not soluble in water except aromatic hydrocarbons (benzene and toluene) which are slightly soluble but are volatile and ripped off by evaporation (10 to 1000 times) (NRC 2003; ITOPF 2011; Scholz et al. 2012). Dissolution of hydrocarbons does not make any significant contribution to oil removal from sea surface because of concentration hydrocarbons that will dissolve in seawater (ITOPF 2011).

Photo-oxidation process is a process that converts aromatic compounds in crude oil to polar species. This process increases the amount of crude oil component susceptible to biodegradation. (Dutta and Harayama 2000) This process is stimulated by sunlight, while hydrocarbons are exposed to oxygen leading to the formulation of soluble products or tars (NRC 2003). Photo-oxidation is dependant spectrum and strength of incident light, optical properties of the water surface as modified by hydrocarbons and other components, hydrocarbon optical properties, and photo-quencher and activator compounds (ITOPF 2011). The Arctic region has a wide range of daylight hours depending on the season, therefore, photo-oxidation is much better in the summer than winter season which has less daylight (Board et al. 2014). The process occurs during the whole period of the spill but is less significant on dissipation compared to other weathering processes; however, the breakdown of oil films under intense sunlight is under 0.1% per day. During the oxidation process, viscous oils with very thick layers and water-in-oil emulsions oxidize to insistent residues than degrading. They then form higher molecular compounds by creating a protective surface area and they are seen as tarballs stranding on shorelines. These tarballs consist outer crests of oxidized oil and sediment particles that surrounds soft and minimum weathered interior. (ITOPF 2011)

Biodegradation process is the process by which naturally occurring bacterial and microorganisms eat hydrocarbons to use them as a food source (Scholz et al. 2012). Biodegradation process can only happen in water and oil interface. Microorganisms are found in seawater and are capable of metabolizing oil compounds, thus the dissolution of materials chemically. The microorganisms in the seawater include; yeast, bacteria, fungi, unicellular algae, protozoa and moulds. (ITOPF 2011; Scholz et al. 2012). These organisms use the oil as carbon and energy source as they breakdown and produce carbon and water as compounds after biodegradation (Margesin and Schinner 2001; Prince and Clark 2004; ITOPF 2011). Each microorganism has its own work of degradation to do, thus degrade specific hydrocarbon group, however, a wide range of microorganisms coming together for continues degradation to achieve successful breakdown. Not all compounds are able to breakdown and as a result, change the oil colour to black. (ITOPF 2011) Nutrients availability, temperature, and oxygen availability promote **biodegradability** while microbial population growth is also dependent on composition, state, and oil concentration. Dispersion increases the rate of degradation by the increase of surface area for better microbial attacks but oil dispersion is less in the Arctic marine environment due to ice and cold condition of water, less wind, current and waves. This eventually affects the rate of degradation since the surface area increase will be minimal. (ITOPF 2011; Lee et al. 2011). In the Arctic and highly saline environments (sea ice brine channels), there are natural indigenous microbial organisms that exist (Scholz et al. 2012). Studies have been conducted on biodegradation of crude oil under Arctic condition using indigenous microbe and the results show that biodegradation was significant in all the treatments even at -1 °C (McFarlin et al. 2011a; 2011b). Another research conducted showed also significant oil biodegradation (Hazen et al. 2010; Lee et al. 2011; Niu et al. 2014). Biodegradation is, therefore, possible in the Arctic marine environment.

4 OIL SPILL RESPONSE TECHNOLOGIES: APPLICATION OF SORBENTS

4.1 Overview of primary and secondary oil spill response technologies

Oil spill response technologies can be divided into five categories. Out of these methods, three of them are primary and two of them are secondary methods. The secondary OSR methods consist of physical and biological methods while the primary methods include mechanical, thermal and chemical countermeasures. The primary OSR methods are used as first-hand clean-up response before the secondary methods are applied. Thermal method is frequently applied as in situ burning since 1960 to burn oil where the spill has occurred. Dispersants are also widely used as chemical methods and another alternative to the mechanical methods in the Arctic. The mechanical OSR technology uses mainly floating to recover oil. Booms and skimmers are typically applied for mechanical OSR. These methods have been used since 1950 and they have been widely accepted across the Arctic environment. (Lampela 2011; Ghaly and Dave 2011; ITOPF 2014) Secondary OSR methods consist of physical methods such as sorbents and biological methods. Biological OSR methods are rarely used in the Arctic environment. However, biological OSR is mostly applied for the removal of stranded oil. (Ghaly and Dave 2011; Brakstad et al. 2015; Li et al. 2016) This study focuses on physical OSR methods, especially the application of sorbents. The focus will be on various absorbent materials and forms and their application in oil spill clean up at harbours. Sorbents are used to clean traces of spilled oil on land and water. Usually, the choice of absorbents in the clean-up process is dependent on factors including; sorbent availability, cost and its safety.

4.2 Application of sorbents

The intensity and location of oil spill determine the clean-up method that need to be applied. Sorbents are usually employed as the final cleanup of oil spill leftovers at offshore and are mostly good for minor oil spills. (Fingas 2011) Sorbent materials serve as a suitable resource for OSR, which recovers oil in a way that is difficult for other technologies (ITOPF 2012a). The performance of sorbent is dependent on the sorbent type and its properties (Potter 2008). Furthermore, sorbents are used in moderation to reduce secondary problems associated with contamination, retrieval, storage and disposal (ITOPF 2012a). They also have a high oil recovery efficiency (Bayat et al. 2005). Some

sorbents are also modified with oleophilic and hydrophobic agents to improve their capacity to absorb oil (Adebajo et al. 2003).

Presently, over 200 sorbents materials are produced and are in use as absorbents for oil absorption (Eyu et al. 2014). However, for a material to be used as absorbents, it should be able to absorb the oil preferentially to that of water and should be both oleophilic and hydrophobic (Aljammal and Juzsakova 2016; Laitinen et al. 2017; Liu et al. 2017; Mahfoudhi and Boufi 2017). Absorbents are not suitable for use in the open sea and cannot typically function well with highly viscous oil (heavy oils, weathered and emulsified oils). However, some absorbents have been designed for such viscous oils. (Ghaly and Dave 2011; ITOPF 2012a; Aljammal and Juzsakova 2016)

Oil sorption can happen in two ways, namely by absorption and adsorption. In the adsorption process, the oil is favourably engrossed to the surface of the material while the absorbent integrates the oil or absorbents allows the oil to penetrate into the open spaces in the material. (Sayed et al. 2004; Kyzas and Kostoglou 2014; Aljammal and Juzsakova 2016). For a successful absorption process, the oil must be able to wet the sorbent material, and this will happen if the surface tension of the liquid is smaller than the critical surface tension of the solid. This means that the critical surface tension of the absorbent should be below that of water and beyond oil. For example, seawater has a surface tension of about 60-65 mN/m and that of oil varies but is mostly in the region of 20 mN/m. (ITOPF 2012a)

According to Fingas (2011), synthetic sorbents are typically reusable but regeneration costs can be high compared to the price of a newly made sorbent. Natural and synthetic materials have critical surface tension values. Inorganic materials, which do not have the required critical surface tension value can be modify with surface treatments, including as heating, to produce the desired condition. For instance, sorbent foams and loose fibres can have their oleophilic characteristic improved when they have been wetted or primed with oil initially. (ITOPF 2012a; Liu et al. 2017) Sorbents ability to retain oil contributes to the effectiveness and performance (Mahfoudhi and Boufi 2017).

4.2.1 Forms of absorbents

Absorbent materials can be categorized into four forms in accordance with their composition and intended use. They include:

- bulk sorbents (loose materials, in a form of particulate);
- enclosed sorbents (in a mesh as booms or pillow);
- continuous sorbents (as mats, sheets, booms or rolls);
- fibre sorbents (loose fibres joined to form snares or sweeps)

(ITOPF 2012a; Federici et al. 2014).

Sorbent booms are loose materials, which are usually enclosed in fabrics, mesh or nets to form booms. They are easy to deploy, control and easier to recover. In some situations, sorbent booms are used to collect thin oil films while their usage ought to be strongly controlled. (ITOPF 2014) In addition, sorbent booms can degrade within hours due to environmental factors such as wave action or abrasion on rocks. The strength of sorbent booms, in particular, enclosed loose materials, is based on the durability of the retaining net material, which can break open in opposing environmental condition. They are usually produced using organic and inorganic natural materials. Sorbent in bulk are loose sorbents and are deployed for small spills due to difficulty in controlling and retrieval, therefore, their use is limited in the marine environment. Continuous sorbents are made up of cylindrical and flat booms with a greater homogeneity. The cylindrical sorbents have a lower surface area with less oil penetration while the flat sorbents have a high surface area to volume ratio. They are usually manufactured from synthetic materials such as polypropylene and woven. While the other forms are effective in a wide range of oils, loose fibre sorbent is less efficient in recovery of more weathered and high viscosity oils. However, bundles of loose sorbent fibers are required to guarantee the recovery of these oils through a combination of adhesion and cohesion. Usually, strips of polypropylene are used to produce and attached together to form snares (pom poms). (ITOPF 2012a)

4.2.2 Characteristics of absorbents

On a whole, absorbents characteristics must be well thought out when selecting an absorbent for oil spill clean-ups, in addition, the oil types must also be considered when choosing the material. Absorbent ability to take up more oil and it being effective is affected by factors including **buoyancy**, saturation, **oil retention**, strength and durability, sorbent fermentation in water and cost. (Teas et al. 2011; TOPF 2012b; Aljammal and

Juzsakova 2016) For absorbents to be effective on floating oils, they need to have high buoyancy and continue to submerge even when it is saturated with water (Liu et al. 2017). Materials such as straw and sawdust have initially a good buoyancy but when they are saturated with water, they start to sink (ITOPF 2012a). The critical parameters to consider for selecting the absorbents are (Teas et al. 2001; Rotar et al. 2014; Aljammal and Juzsakova 2016):

- **Rate of absorption:** Absorption is faster when the oil is lighter (e.g. are diesel, gasoline, and benzenes).
- **Absorption capacity:** The amount of pollutant that is absorbed onto the absorbent per mass of absorbent
- **Rate of adsorption:** Rate of adsorption depends on the type of oil. The thicker the oil, the more it adheres to the adsorbent surface.
- **Oil retention:** Oil weight causes sorbents structure to drop and deform. In this case, when the sorbent is elevated out of the water, the oil that is trapped in the pores can be released. With lighter and less viscous oils, oil is lost easier through the pores.
- **Ease of application:** Application of sorbents both in a manual and in mechanical. For example, clay and vermiculite can cause dusting in windy condition.
- **Kinetic model:** Kinetic model describes the absorption process and measures the diffusion of adsorbate in the pores (Teas et al. 2001; Rotar et al. 2014; Aljammal and Juzsakova 2016)

4.2.3 Limitations of absorbents

Absorbents have limitations in terms of oil clean-up. The following are some limitations of absorbents;

- Environmental conditions (wind, wave, and current) affect absorbent ability to retain oil.
- They are less effective with highly viscous oils.
- Cost of regeneration is often higher than the cost of newly produced absorbents
- Long stay in water affect the composition and efficiency of some absorbents. This causes problems with recovery and storage of oil.
- One largest limitation is their collection from water surface, which is always difficult. (ITOPF 2012a; Aljammal and Juzsakova 2016).

4.3 Classification of absorbents

4.3.1 Absorbent materials

Sorbent materials can be derived from renewable resources, which are often cost-effective and can potentially be reused (Ghaly and Dave 2011; ITOPF 2012a; Aljammal and Juzsakova 2016; Laitinen et al. 2017; Liu et al. 2017; Mahfoudhi and Boufi 2017). Solid sorbent materials serve as absorbents to absorb liquid through diffusion by a similar procedure to capillary action. The material combines with the liquid (oil), get swollen so that there is no leakage out, even under severe pressure. The absorbents are typically prepared from synthetic polymers to obtain high surface area to facilitate absorption. (Adebajo et al. 2003; ITOPF 2012a) Figure 7 shows some of the most frequent used absorbents used for oil absorption. For the purpose of this study, bio-based absorbents will be explored, especially the focus is on cellulose based absorbents.

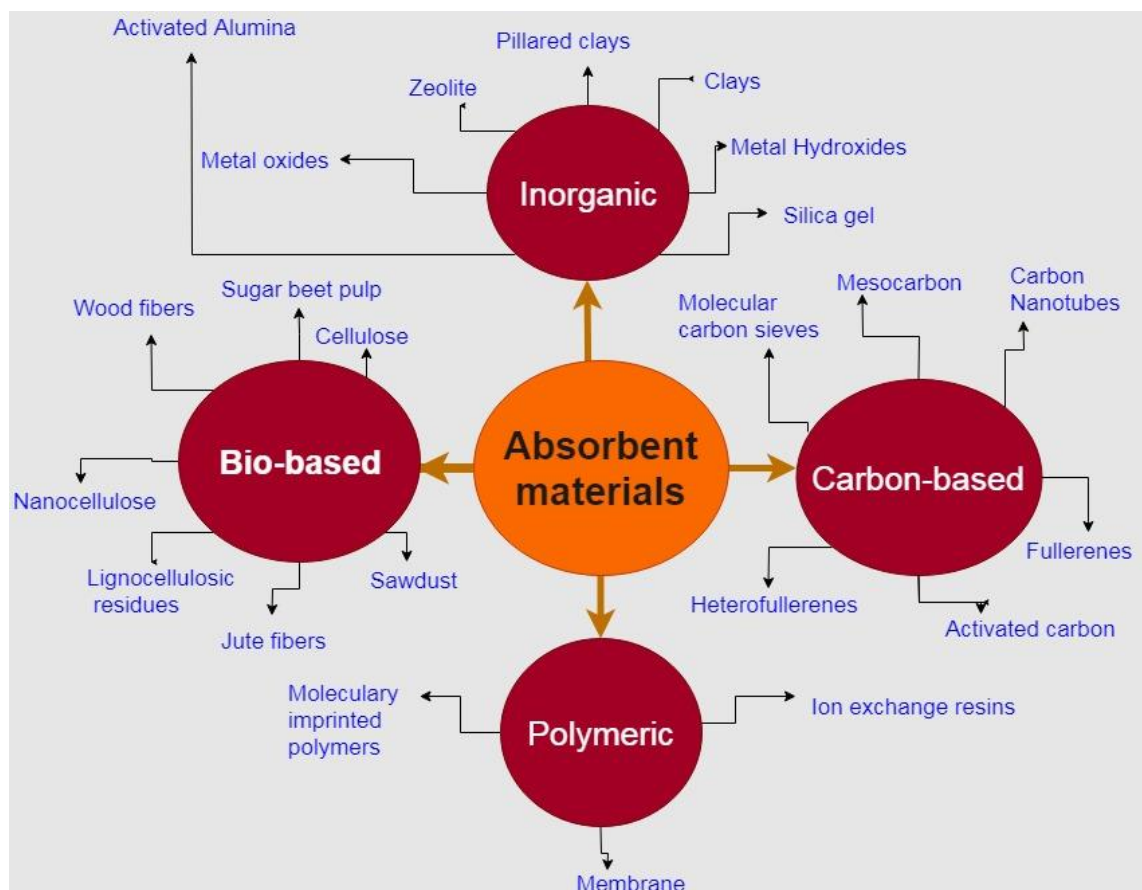


Figure 7. Most frequently used absorbent materials for absorption. (Adapted from Mahfoudhi and Boufi 2017).

Generally, several important factors such as porosity, **hydrophobicity**, appropriate pore spaces and surface area of the absorbent are considered in the separation process. The surface area of absorbent is very important and essential for the efficient removal of oil from water. (Aljammal and Juzsakova 2016; Laitinen et al. 2017; Liu et al. 2017) Furthermore, materials with high carbon or oxygen content have a good recovery efficiency of oil from water. Nevertheless, not all materials meet all prerequisites for selectivity, rate of sorption, capacity rate and recycling rate. Absorbent materials used for absorption include materials such as sawdust, peat, bark, paper-pulp, bagasse, cork, feathers from chicken, straw, human hair and wool, vermiculite and pumice, polypropylene, polystyrene, polyester foam and etc. (Teas et al. 2001; Ghaly and Dave 2011; ITOPF 2012a; Aljammal and Juzsakova 2016; Liu et al. 2017). They can be categorized into groups such as; organic and agro-based products, synthetic materials and inorganic materials as shown in Table 3. (Deschamps et al. 2003; Lim and Huang 2006; Aljammal and Juzsakova 2016) The very recent advances in absorption process have also brought into existence nanotubes and nanoparticle absorbents for oil absorption (Gu et al. 2014).

Table 3. Absorbent material and their advantages, and drawbacks (Adapted from Aljammal and Juzsakova, 2016).

Raw material	Advantages	Disadvantages
Natural organic		
Agricultural sources and residues such as lignin; activated carbons after pyrolysis. Natural fibre material such as cotton fibres and corn stalk, bagasse pith and nonwoven wool.	Environmentally friendly. Biodegradable. Non-toxic. Not corrosive. Low cost. Able to be recycled. Easy to dispose.	Low sorption capacity. Hydrophilic in nature. Can have high water absorption, resulting in loss of sorbent buoyancy.
Synthetic Polymer		
Synthetic polymers such as polyethylene, butyl rubber, polyurethane and polypropylene.	Widely used because of their hydrophobic and oleophilic characteristics. Some types are reusable.	They are non-biodegradable. They are not naturally occurring as mineral products.

Table 3 (Continued)

Raw material	Advantages	Disadvantages
Inorganic minerals		
Perlite, graphite, vermiculites, solvent clay and diatomite, vermiculite exfoliated graphite, sepiolite and zeolites.	Very high oil absorption capacity. The sorbent can also be regenerated.	Very sensible to fouling. Susceptible to aging process. High water absorption. Low buoyancy, making it difficult to recycle.
Nanotube and Nanoparticles		
CNTs, Co-polymer made of improved carbon nanotubes (MWCNT), Granulated NaA zeolite nanoparticles improved with hexadecyltrimethylammonium bromide and Magnetic carbon nanotube sponges (Me-CNT sponge).	Exceptional one-dimensional structure. Large surface area. Oleophilic and hydrophobic in nature.	Poor solubility and process ability rate restricts their application. They may pose a risk for the environment.

Natural organic sorbents are carbon-based materials obtained from abundant and affordable biomass from plants or residues from animals (Ruiz et al. 2011). Bio-based absorbents are of low cost, easy to obtain and are of renewable sources. These materials can be formed into various forms of absorbents (sheets, booms, pads, and filter and fibre assemblies). Their oil sorption capacity is typically 3-50 times their own weight and they have less density compared to inorganic and synthetic absorbents. (Ruiz et al. 2011; Laitinen et al. 2017) Recently cellulose which is the main structural constituent of many of plants materials has been under special consideration for oil clean-up (Aljammal and Juzsakova 2016).

Synthetic polymer oil sorbent such as polyurethane foam, nonporous polystyrene fibres, polypropylene nonwoven web, and macroporous rubber gels and polypropylene fibres are commercial sorbent types used in oil spill clean-up. They have oleophilic and hydrophobic properties. (Lin et al 2010; Karana et al. 2011; Laitinen et al. 2017) They are not biodegradable which makes them not friendly to the environment. The most commercially used synthetic materials are polypropylene and polyurethanes. Synthetic materials have their absorbing capacity to be 70 to 100 times their own weight. This is due

to their oleophilic and hydrophobic properties. These materials are also available in sheets, rolls or booms and can also be applied to water surface as powders. (Choi and Cloud 1992; Teas et al. 2001; Deschamps et al. 2003; USEPA 2010)

Inorganic oil sorbents such as clay, charcoal, and zeolite, fly ash, silica nanoparticles, amorphous silica, and silica aerogels are typically termed as “sinking sorbents”. They are fine-grained and highly dense materials. (Babel and Kurniawan 2010; Aljammal and Juzsakova 2016; Laitinen et al. 2017) . Furthermore, these natural materials are cheaper, abundant for use and supply. Several studies have shown that inorganic sorbents can be modified to enhance their oil sorption capacity. (Bandura et al. 2015; Laitinen et al. 2017) Ghaly and Dave (2011) reported that inorganic sorbents absorbing capacities are 4-20 times their own weight. In addition, these materials are more attractive than synthetic materials because of their availability, even though, they are poor in oil-water selectivity (ITOPF 2012a).

Carbon nanotubes (CNT's) have gained attention due to their excellent absorption capacity. CNTs are very good absorbents with high hydrophobicity. (Gui et al. 2013) A recent report by Gu et al. (2014) shows that CNT absorbents have a good ability to absorb oil from water. In addition, the absorbents are able to retain oil after retrieval and can be reused. Carbon materials have excellent absorption capabilities, high selectivity, highly recyclable and can be modified to absorb oil and then prevents water absolutely. Furthermore, carbon-based absorbents have high surface area, low in density, extraordinary mechanical characteristics, good chemical stability, environmentally friendly and huge pore volume. (Aljammal and Juzsakova 2016)

4.3.2 Cellulose-based materials

Cellulose is the most abundant biopolymer, which can be found in plants. It provides plant rigidity or firmness. In addition, it is a raw material used, e.g. in a form of paper and board, wood and textile fibres (cotton or flax). (Klemm et al. 1998) Cellulose exists in a form of **semi-crystalline polymer**, comprising of both crystalline and amorphous phases. It is a linear polymer and contains three hydroxyl groups in its structure. Furthermore, due to strong hydrogen bonds between its chains, it does not dissolve in water and other solvents. (O'Connell et al. 2008) The shape of cellulose is a **ribbon-like** that allows it to bend (Klemm et al. 2005; O'Connell et al. 2008).

Cellulose is obtained from wood, plants, microbes, and animals. They include seed fibre (cotton), wood fibres (both soft and hard kinds of wood), bast fibres (flax, jute, ramie, and hemp), grasses (bagasse, bamboo), algae (*Valonica ventricosa*) and bacteria (*Acetobacter xylinum*). (Hokkanen et al. 2016) The percentages of cellulose in the raw materials differ from each other as shown in Table 4. The most common raw materials for commercial cellulose production are wood and cotton (Klemm et al. 2005).

Generally, most plants cell walls are made up of cellulose. Wood and lignocellulosic materials are known for their mechanical properties, especially they have high **mechanical strength** and can undergo large dimensional changes because of shrinking and swelling (Dumitriu 1996, p. 87). Currently, there are significant interests towards cellulose nanomaterials including nanocrystals, nanofibrils, and microfibrils (Siró and Plackett 2010). Cellulose-based materials can be used as economical absorbents but their performance is varying depending on the form of cellulose. Pure cellulose has a surface area of 1.64 m²/g, pore volume of 0.00839 cm³/g and pore diameter of 20.41 nm. (Šćiban et al. 2006; Gurung et al. 2014)

Table 4 Percentages of cellulose in cellulose raw materials (Adapted from Klemm et al. 1998).

Cellulose raw material	Percentages (% wt) of cellulose
wood	40-50
leaf fibres and sisal fibres	55-73
bast fibres and flax	70-75
hemp	75-80
jute	60-65
ramie and Kapok	70-75
kenaf	47-57
canes and bamboo	40-55
cottonseed hairs (purest source)	90-99
rice	43-49
cereal straw	48
wheat	49-54
rye	50-54
bagasse	33-45
oat	44-53

Typically, the absorption capacity of cellulose can be improved by chemical modifications. Some of these chemicals include organic and mineral acids, bases, organic compounds, and oxidizing agents. (Siró and Plackett 2010; Klemm et al. 2011; Moon et al. 2011; Dufresne 2013) Chemical modification of cellulose is possible due to large number of hydroxyl groups. The modification methods can be grouped into two main streams i.e. monomer-grafting and direct modification. Monomer grafting attach wide range of specific groups to the cellulose backbone while direct modification attach functional groups to hydroxyl groups of cellulose backbone through base solutions, organic and mineral acids, organic compounds, and oxidizing agents. (O'Connell et al. 2008; Ngah and Hanafiah 2008)

4.4 Aerogel as oil absorbents

Aerogels are nanoscale mesoporous solid materials produced by replacing the liquid in the gel with air. They are quick to absorb large amount of oil and they can still float on water. This is because of large surface area, high porosity and low density of aerogels. (Nakagaito et al. 2013)

Cellulose aerogels have additional advantage of naturally occurring cellulose including, abundant sources, biodegradability, recyclability rate and simplicity to surface modification) as an advantage. Due to this, they are considered as one of the most attractive green sorbent materials. (Innerlohinger et al. 2006; Cai et al. 2008; Gavillon and Budtova 2008). The cellulose aerogels can be categorised as those derived from cellulose and its derivatives, those based on regenerated cellulose (RC), and nanocellulose-based aerogels (Tan et al. 2001; Cai et al. 2012; Nguyen et al. 2014; Wan et al. 2015).

Cellulose aerogels are typically fabricated by freeze-drying method, in which, **gelation** (solidification by freezing) is a very important process. During solidification by freezing, a three-dimensional cellulose network is formed. The gelation formation can be classified into physical and chemical **cross-linking** mechanism. The physical cross-linking is used in the case of RC aerogels and nanocellulose aerogels. (Nguyen et al. 2013; Jiang and Hsieh 2014) The chemical gelation mechanism needs additional cross-linking agent (paper-strengthening resin) to be added to induce the formation of cross-linked cellulose network (Feng et al. 2015; Meng et al. 2015).

RC based aerogels are manufactured through dissolving the cellulose into a required solvent, regeneration of cellulose by exchanging of solvent by nonsolvent, and then drying the attained aerogels. During these process steps, the used sorbent can be harmful and the process is time-consuming. (Jin et al. 2004; Gavillon and Budtova 2008) The oil-sorption performance of aerogel is largely dependent on density and viscosity of the oil, **capillary effect, van der Waal forces**, hydrophobic relations amongst oil and absorbents and aerogels morphological parameters including surface wettability, total pore volume and its structure. Typically, oils with low viscosity penetrate in the porous network of the aerogels more easily, and, therefore, higher absorption capacity is achieved. (Choi and Cloud 1992; Gui et al. 2011; Meng et al. 2015; Wang et al. 2013)

Cellulose aerogels have different kinds of pore structures and the pore structure greatly depends on drying process used. Typically, freezing and supercritical drying process are used. For example, supercritical carbon dioxide drying successfully avoids the three-dimensional porous structure from collapsing and results in aerogels with low density and a higher surface area. Highly porous aerogels have high oil-absorption capacity. (Tan et al. 2001; Fischer et al. 2006; Sehaqui et al. 2011; Kobayashi et al. 2014)

One notable disadvantage of supercritical drying is its cost, which limits its industrial-scale usage (Liu et al. 2017). The freeze-drying technique is safer, more economical and environmentally friendly, which can replace the traditional supercritical drying (Fumagalli et al. 2013; Jiang and Hsieh 2014).

4.4.1 Nanocellulose-based aerogels oil absorbents

Nanocellulose based oil sorbents have been recently established to overcome the challenges of RC aerogels. Nanocellulose are referred to as novel cellulosic materials with typical lateral dimension ranging from 2-6 nm. (Klemm et al. 2011; Dufresne 2013) Nanocellulose, a new class of bio-based absorbent is lightweight, has strong mechanical strength, high specific surface area, is environmentally friendly and can easily be modified (possibility of surface modification). Aerogel based nanocellulose as absorbents has high absorption capacities and a very good binding attraction compared to other counterparts at the macroscale. Furthermore, at the nanoscale, there is the emergence of additional criteria due to its small size, specific surface expansion and the dominance of interfacial phenomena. (Zhou et al. 2011; Mahfoudhi and Boufi 2017)

Based on cellulose sources, functions and its preparations, nanocellulose can be grouped into three categories, namely; Cellulose Nanocrystals (CNC), Cellulose Nanofibrils (CNF) and Bacterial cellulose (BC) (Siró and Plackett 2010; Klemm et al. 2011). Characteristics of these three kinds of Nanocellulose are stated in Table 5. By comparing nanocellulose to RC, nanocellulose exhibits the structure of cellulose (I), having greater strength or stiffness and larger specific surface area. In addition, the resultant aerogels of nanocellulose shows higher mechanical strength than RC aerogels after freeze-drying. (Jin et al. 2004; Gavillon and Budtova 2008)

CNFs consists of long, flexible and entangled network of cellulose nanofibres with a diameter of 2-60 nm and a length of several micrometres (Klemm et al. 2011; Dufresne 2013). CNFs comprises of individual and aggregated nanofibrils, which are made of alternating crystalline and amorphous cellulose areas and therefore, the unique **morphology** gives CNF-based aerogels greater flexibility and an ordered porous structure over RC aerogels (Lindström and Winter 1988, as quoted in Liu et al. 2017).

“Nanocrystalline cellulose (CNC) comprise rod-like cellulose crystals of a width and length (5-70 nm) and between 100 nm and several microns” (Liu et al. 2017). CNC has a greater degree of **crystalline** and shortfall in aspect ratio, compared to CNF and BC, which have a three-dimensional cellulose nanofibres network. Furthermore, the aerogels from CNC has poor mechanical properties compared to CNF and BC and CNC are usually not employed as oil sorbent materials. (Liu et al. 2017)

Currently, cellulose aerogels (cellulosic sponges or foams) based on cellulose nanofibrils (CNFs), which are highly porous and ultralow in density have come of interest. CNFs can be renewed, have good mechanical properties, low density, high porosity, natural biodegradability and environmental friendliness (Sai et al. 2013; Gupta and Tai 2016; Laitinen et al. 2017). All these characteristics increase the potentials CNF aerogels for being used as oil and chemical sorbents (Laitinen et al. 2017). Laitinen et al. (2017) used a straight forward process to develop low cost, **ultralight**, porous, hydrophobic and recyclable cellulose nanofibril aerogels, which is obtained from recycled waste fibres. The CNF aerogels obtained excellent oil-water selectivity and high absorption capacity of oil (marine diesel oil, kerosene, gasoline, motor oil, castor oil, and linseed oil) and with other organic solvents such as dimethyl sulfoxide, chloroform, n-hexane, toluene, acetone, and ethanol. After the absorption process, oil was recovered mechanically by squeezing and the superabsorbent aerogel could be used again more than 30 sequences.

The CNF aerogel displayed excellent absorption capacity (142.9 g/ g of diesel oil) compared to polypropylene-based material (8.1-24.6 g/ g of diesel).

Table 5. Characteristics of CNF, BC and CNC kind of nanocellulose (Adapted from Liu et al., 2017)

Nano-cellulose	Sources	method	Chemical Composition	Structure	Crystallinity	Yield	Cost
CNF	Wood, sugar beet, potato tuber, hemp, flax	Mechanical pressure and refining, chemical or enzyme treatment	Contains residues of hemicellulose	Entangled network-like	low	high	low
CNC	Wood, flax, cotton, hemp, wheat straw, mulberry barks, ramie	Acid hydrolysis from a different cellulose source	No amount of hemicellulose	Rigid and rod-like	high	low	high
BC	Bacterial cellulose, and microbial cellulose	Bacterial synthesis (Acetobacter species)	Pure cellulose without hemicellulose, lignin, and pectin	Ribbon-shaped fibrils (width = 25-100 nm)	high	low	high

Another CNF aerogel oil absorption capacity (88 to 228 g/ g) has been reported by Wang et al. (2016). The oil recovery method, recyclability of absorbent, and cost using CNF aerogels are much cheaper than those of carbon-based absorbents. One challenge of CNF aerogels are their development at low cost and remaining efficient. (Laitinen et al. 2017).

CNF based aerogels are typically produced using freeze-drying process (Korhonen et al. 2011). Korhonen et al. (2011) prepared hydrophobic nanocellulose aerogels by freeze-drying of CNF hydrogels to test its reusability property. The highly porous and low-density aerogels showed high water-repellent characteristics. The oil did not drain out of from the aerogel when it was withdrawn from the water and the aerogel remained floated on the water surface. The absorption capacity of CNF aerogel did not reduce. The CNF aerogel showed good reuse character after 10 times absorption of organic solvent, drying, and re-absorption cycles. Xiao et al. (2015) also prepared hydrophobic aerogel by chemical vapour deposition. The aerogel absorbed oil 52 times its own weight.

CNFs can be mixed with other polymers to formulate hybrid aerogels, which can be used as oil sorbents. They show super-hydrophobic and super-oleophilic characteristics and an excellent absorption capacity for different oils. The hybrid aerogel have also very good mechanical and elastic toughness, therefore, making them potential for oil spill clean-up. (Zheng et al. 2014)

4.4.2 Bacterial cellulose aerogels as absorbents

Bacterial cellulose (BC) are made up of nanofibrils. They are obtained from certain types of bacterial (acetic acid bacterial), which involve enzymatic **polymerization** of glucose via bottom-up approach. BC aerogels have high degree of crystallinity, polymerization, mechanical stability and water retention properties with reference to CNF. (Klemm et al. 2011) Oil sorption capacity of BC aerogels can be brilliant by the preparation of hybrid structure which contains graphene (Wang et al. 2014). Graphene aerogels have demonstrated good absorption abilities and reuse characteristics due of its low density, higher aspect ratio, excellent elasticity and strong mechanical characteristics (Bi et al. 2012; Nguyen et al. 2012; Zhao et al. 2012). By incorporating graphene oxide (GO) into BC suspension produced ultralight and highly porous BC/ reduced GO (rGO) hybrid aerogels by drying-freezing process and thermal reduction in H₂. Comparing pure BC aerogels (amphiphilic), BC/ rGO aerogels organic solvents selectivity and absorption capacity for the organic liquids were very high (135-150 g/g). (Wang et al. 2014)

4.4.3 Carbon aerogels as absorbents

Carbon aerogels are oil sorbent materials that have excellent absorption abilities, intrinsic hydrophobic and oleophilic nature and both thermal and chemical stability. **Pyrolyzing** resorcinol formaldehyde organic aerogels in an inert atmosphere form a cross-linked carbon structure, which produces carbon aerogels. (Pekala 1989; Wu and Fu 2008) These aerogels have a high density (100-800 g/cm³) (Fu et al. 2003; Wu et al. 2004). On the other hand, carbonization of biomass materials is simple, inexpensive and no chemicals involved in its preparing process. In addition, carbon aerogels are eco-friendly and sustainable. Nanostructured carbon aerogels resulting from nanocellulose meet the expectations of a higher specific surface area, high porosity and greater mechanical property. Carbon aerogels originates from CNF and BC. (Liu et al. 2017)

EXPERIMENTAL PART

5 MATERIALS AND METHODS

5.1 Materials

Material used for the CNF production was recycled box board, which was obtained from board-container collections. The pulp was initially pulped without chemicals by using Kenwood KM020 pulper, United Kingdom. Consistency of pulp was 15%, temperature of 45°C, rotor speed of 2 ms⁻¹ and a pulping time of 10 mins. The pulp was washed and screened after pulping using Somerville screen. (Laitinen et al. 2017)

The washed pulp was fibrillated with a Masuko super masscolloider grinder MKCA6-2J (Japan) to obtain board nanofibrils. For this purpose, the fibrous board material was diluted with water to a 1.5% consistency. The grinding discs of the Masuko grinder were first carefully brought into close contact, which was verified by the low friction sound. Then, the treated cellulose was passed twice through the grinder using the zero grinding discs gap, after which the discs were adjusted to negative gap values. The board pulp was passed through the grinder a total of 14 times, using negative gap values of 3 times -20 µm, one-time -40 µm, one-time -50 µm, one-time -60 µm, 3 times -80 µm and 5 times -90 µm to obtain different board nanofibers (i.e. CNF suspension).

Methyltrimethoxysilene (98%, MTMS) was obtained from Evonik Industries, Germany, and Hexadecyltrimethoxysilane (>85%, HDTMS) acquired from Sigma-Aldrich, Germany. In addition, light-weight marine diesel oil was acquired from Neste, Finland and Mobil DTE™ 20 Series hydraulic oil from a local supermarket. All the chemicals were used without any purification. A 4 connect nylon black 12/ 25 mm diameter 10 m Sleaving material was obtained from Motonet, Finland. A commercial oil absorbing material (polypropylene) from inside oil-absorbing boom was obtained from local rescue service.

5.2 Fabrication of hydrophobic cellulose nanofiber aerogels

Firstly, CNF suspension was diluted with deionised water to a consistency of 1.5%. Ultra-Turrax system was set to 8000 rpm for 30s and used to homogenise the suspension. Furthermore, pH was adjusted to 4 by using a 0.5 M HCl solution. Secondly, silane solutions (20 wt %) used for the hydrophobization of CNF were prepared separately. MTMS and HDTMS were diluted in ethanol and after the dilution, the silane solutions were mixed with a magnetic stirrer for 10 mins. Then 25 wt% of the prepared saline

solutions were added to CNF suspension at a ratio of 50/50% and suspension was stirred with a magnetic stirrer for 2 h at room temperature (Figure 8a).

The silylated CNF suspensions were put into a plastic tube (volume of 15 ml), and then frozen in a liquid nitrogen at a temperature of -196°C before they were transferred into a vacuum chamber of freeze-drying device (Scanvac cool safe 55-15 Pro, Denmark) for one week (168 h) (Figure 8b and c). The cooling chamber temperature was set to -54°C to acquire hydrophobized CNF aerogels (Laitinen et al. 2017). Right after the drying-freezing, aerogels were transferred into an oven to ensure curing at a temperature of 100°C for one day (24 h). The prepared CNF aerogels are presented in Figure 8d.



Figure 8. A) Illustration of CNF suspension stirred on a magnetic stirrer. B) CNF suspension frozen in a liquid nitrogen. C) Freeze-drying to obtain hydrophobized CNF aerogels. D) Prepared CNF aerogels.

5.3 Sorption of oils using aerogels

WEISStechnik environmental simulator (climate chamber) was used to create artificial Arctic environment conditions to simulate marine environment in Oulu and Tromsø ports by setting the temperature in the climate chamber to 0°C and humidity to 5%. A shaking machine (IKA, KS 260 basic) was used to create a shaking effect. Figure 9 shows the experimental set-up used for the study.



Figure 9. Experimental setup in the WEISStechnik environmental simulator

The oil absorption experiments were carried out using two different types of oils, thus diesel and hydraulic oils. Table 6 shows the properties of the two oils. In addition, norosilicate glass beakers (600 mL) were used as an oil-water container, ice cubes made of 1% salinity were used to simulate ice condition, 3 pieces ice cubes (5.3 cm per one) was added into a beaker using shaking frequency of 100 rev/min. A constant specified amount of oil (10 g) was added to the 600 mL beaker containing 390 mL of water and

then placed on the shaker apparatus (IKA, KS 260 basic). A weighted sorbent wrapped with a sleeving net material was added to the system and shaken for 1 to 60 mins. However, no-shaking condition and no-ice condition were also considered for some experiments. The experimental procedure involved the following stages:

- Setting the desired temperature of the climate chamber (0 °C) for all the experiments.
- 390 g of water and 10 g of oil was added in the beaker.
- The beaker was placed on the shaker inside the climate chamber.
- Ice cubes (3 pcs) were added to the solution if required.
- The shaking machine was turned on if required.
- The absorbent with sleeving protection was placed into the beaker containing oil and water.
- The sorption was continued for 1, 2, 3, 5, 10, 30 and 60 mins.
- The oil-soaked absorbent was removed to the measuring cup and weighted

Table 6. Specification of oil samples used in the experiments (properties and units).

Property	Unit	Oil sample	
		Diesel	Hydraulic oil (Mobil DTE 25)
Density	kg/dm ³	0.826	0.876
Kinematic viscosity at 40 °C	m ² /s		44.2
Kinematic viscosity at 50 °C	m ² /s	1.8	
Flash point,	°C	63.5	
Pour point,	°C		-27

Two water salinity conditions, i.e. 1 and 3.5% salinity levels were used in the experiments. The 1% salinity represented Baltic Sea water of 10 ppt salinity, the 3.5% represented Norwegian Sea water of 35 ppt salinity, and both were used to simulate in different experiments with diesel or hydraulic oil. When the experiment requires shaking condition, the shaker is switched on to simulate shaking condition. Table 7 and 8 shows the designed experimental plan.

Table 7. The experimental plan for 1% salinity condition oil absorption

Shaking	No shaking	Ice cubes	No ice cubes	Oil	Aerogel
X		X		Marine diesel oil	Cellulose-based
	X	X			
X			X		
	X		X		
X		X			Ref (Boom plugs)
	X	X			
X			X		
	X		X		
X		X		Hydraulic oil	Cellulose-based
	X	X			
X			X		
	X		X		
X		X			Ref (Boom plugs)
	X	X			
X			X		
	X		X		

Table 8. The experimental plan for 3.5% salinity oil absorption

Shaking	No-shaking	No ice cubes	Oil	Aerogel
X		X	Marine diesel oil	Cellulose-based
	X	X		
X		X		Ref (Boom plugs)
	X	X		
X		X	Hydraulic oil	Cellulose-based
	X	X		
X		X		Ref (Boom plugs)
	X	X		

5.4 Absorption capacities

5.4.1 Diesel oil absorption using CNF aerogels and commercial reference

Pre-weighed CNF aerogels and polypropylene material (plug) boom together were placed into diesel oil for 1, 2, 3, 5 10 and 30 mins, respectively. Full absorption was obtained after 1-2 minutes in all conditions (Shaking, no-shaking, ice, no-ice, 1 and 3.5% salinity). The mass of the absorbed oil per unit mass of dry absorbent (g) was used to determine the oil sorption capacity (Laitinen et al. 2017). Overall, 72 experiments were conducted for marine diesel oil, with 6 replicated measurements for CNF aerogels and reference materials.

5.4.2 Hydraulic oil absorption using CNF aerogels and commercial material

In absorption test for the hydraulic oil, CNF aerogels and commercial polypropylene material (plug) boom were weighed into a beaker. A high quality and durable nylon protected was used to cover the absorbents. Pre-weighed CNF aerogels and polypropylene material (plug) boom together with the sleeving material were put into hydraulic oil-water solution for 1, 2, 3, 5 10, 30 and 60 mins, respectively. Complete absorption was obtained for both CNF aerogels and polypropylene after 60 mins. Over 84 experiments were conducted for hydraulic oil, with 7 replicated measurements for CNF aerogels and reference materials.

6 RESULTS AND DISCUSSION

6.1 Hydrophobicized cellulose nanofiber aerogels

In the experiments, silylation agents (MTMS and HDTMS) were added before drying-freezing to cross-link (i.e. MTMS) the CNF aerogel to attain a porous structure of CNF aerogel. Thermal post-treatment was used to cure the hydrophobicized cellulose material. The pH of the reaction medium was reduced to 4 to promote hydrolysis of alkoxysilanes and minimise self-condensation (Zhang et al. 2015, Laitinen et al. 2017).

Density and porosity of the manufactured CNF aerogels is a function of CNF suspension consistency. CNF aerogels had a density of approximately 0.01 g/cm^3 at a consistency of 0.75% while the density of polypropylene was 0.0521 g/cm^3 . The porosity of CNF aerogels was 99.15% at 0.75% consistency, while that for polypropylene reference absorption material was 94.26%. Hydrophobic modification by using cross-linking agents forms a continuous sheet-like coating and the porous structure was well maintained in the CNF aerogels. (Laitinen et al. 2017)

Large amounts of hydrophilic hydroxyl groups in unsilylated CNF make freeze-dried, unmodified CNF aerogels unsuitable for oil absorption. A hydrophilic aerogel easily breaks down in water, and the water enters the aerogel to destroys the hydrogen bonds that exist between the CNFs. This causes the collapse of 3D-structure of the CNF aerogels. The silylated aerogels were instead confirmed to be hydrophobic after visual observation, because water droplet rolled off from the surface of the silylated CNF aerogels at an increased descending angle. In addition, water uptake was low.

CNF aerogels had notably higher absorption capacity for both diesel and hydraulic oil in all conditions as shown in Figure 10 and 11. The CNF aerogels had 3-5 times better oil (diesel and hydraulic) absorption compared to polypropylene material in both 1 and 3.5% salinity water. However, this is lower than the absorption capacities of the previous studies (references), presumably due to higher consistency of aerogel. Polypropylene material absorbed some amount of water during oil absorption. Moreover, the commercial reference material in contact with hydraulic oil and fresh ice cubes got frozen, while CNF didn't show this behaviour.

6.2 Oil absorption

6.2.1 Low salinity (brackish) environment (10 ppt)

In the experiments, the absorption of hydraulic oil required more time to obtain fully saturated absorbents than diesel oil as shown in Figure 10. The absorbents were fully saturated with diesel oil 1-3 mins whiles the hydraulic oil required 30-60 mins to obtain fully saturated absorbents. This might have been due to the physical and chemical properties of both oils. Generally, oil absorption is faster with lighter oil products (Aljammal and Juzsakova 2016).

Using commercial material under shaking or no-shaking with icy or no-ice condition, full absorption was obtained in 30 and 60 mins for hydraulic oil. For CNF aerogels, absorption was typically complete between 30-60 mins without shaking. Under shaking and no ice condition, less time was required to obtain almost full absorption for hydraulic oil.

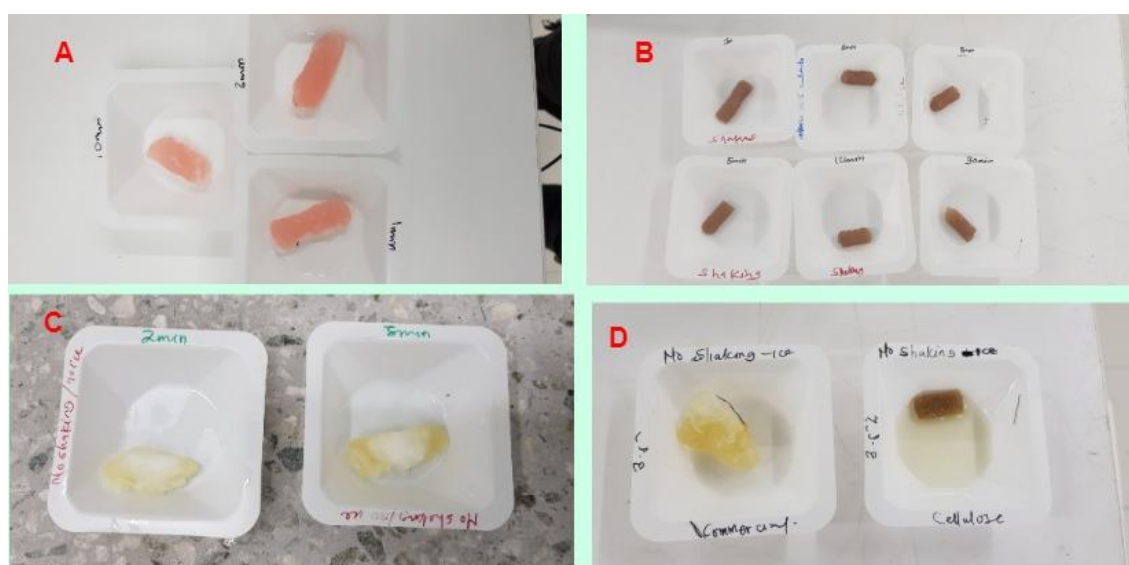


Figure 10. A) Fully saturated commercial material with diesel oil after 1-3 mins B) CNF aerogels full with diesel oil after 1-3 mins C) Hydraulic oil in commercial materials, not full at 1-30 mins D) Hydraulic oil in both materials, full in 30-60 mins.

Figure 11 represents the average values of oil absorption capacities for diesel and hydraulic oil in 1% salinity. These experiments were conducted in icy and no-ice conditions with a pairwise combination of shaking and no-shaking conditions (Table 7). The CNF aerogels obtained a higher absorption capacity of 59.90 g/g for diesel oil and 34.56 g/g for hydraulic oil. The commercial material obtained diesel oil absorption of 15.62 g/g and 13.96 g/g for hydraulic oil. The highest diesel oil absorption was under no-shaking (no-ice) conditions in 1% salinity for both materials. Therefore, diesel oil is absorbed better under no-shaking condition in 1% salinity.

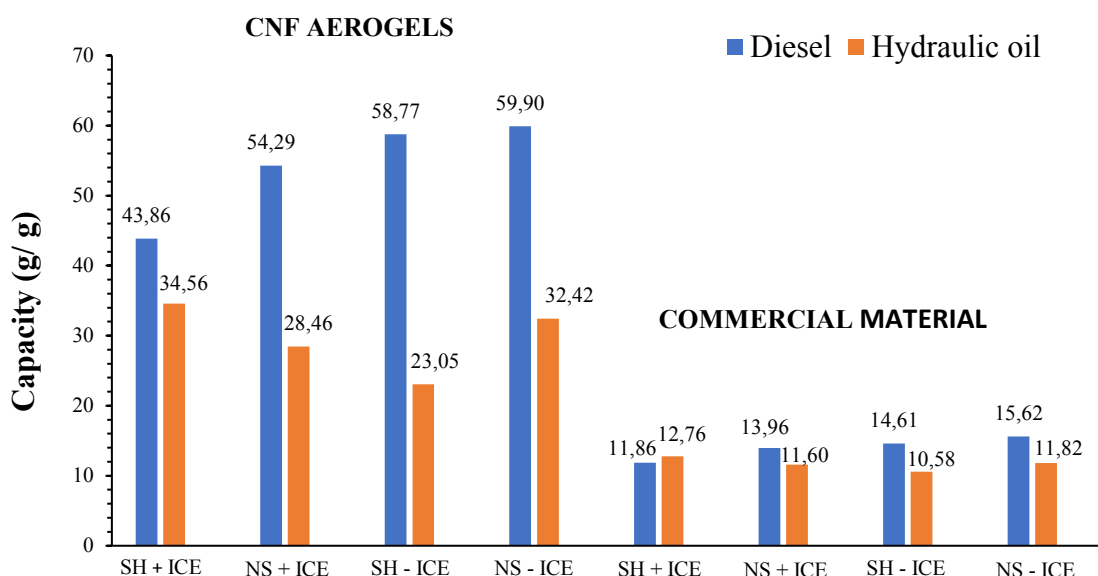


Figure 11. Comparison of absorption of diesel and hydraulic oil in 1 % salinity. SH means shaking condition and NS means a no-shaking condition

Marine diesel oil has a notably higher absorption capacity than hydraulic oil in 1% salinity for both CNF aerogels and reference material. The lower absorption capacity of hydraulic oil was due to its higher viscosity. The higher absorption capacity of the diesel oil could have been due to its lower viscosity. In low salinity (1%), the diesel oil became more hydrophobic due to the electrostatic interaction and the low salinity effect. Because of this, the oil absorption force of the absorbents was then enlarged, and caused increase in absorption capacity of the diesel oil. (Zou et al. 2015; Alaa El-Din et al. 2018).

6.2.2 High saline environment (35 ppt)

The sorbents were fully saturated with diesel oil in 1-3 mins whiles hydraulic oil required 30-60 mins to obtain fully saturated absorbents (Figure 10). This might have been due to the physical and the chemical properties of both oils. Generally, oil absorption is faster with lighter oil products (Aljammal and Juzsakova 2016).

Figure 12 shows absorption capacities for CNF aerogels and commercial materials in 3.5% salinity. These experiments were conducted in no-ice condition with a pairwise combination of shaking and no-shaking conditions (Table 8). Generally, CNF aerogels had higher absorption capacities for both oils compared to the commercial reference material. Shaking condition showed high oil absorption capacity compared to no-shaking condition. Therefore, hydraulic oil is absorbed better under shaking condition in 3.5% salinity.

In all the conditions the experiments were conducted, hydraulic oil showed a notably higher absorption capacity than the diesel oil in 3.5% salinity. The reason might have been due to the high viscosity of the hydraulic oil. In high salinity (3.5%), the hydraulic oil became more hydrophobic due to electrostatic interaction and high salinity effect. This enlarged the absorption force of the absorbents, and thus increased the hydraulic oil absorption. (Zou et al. 2015 and Alaa El-Din et al. 2018)

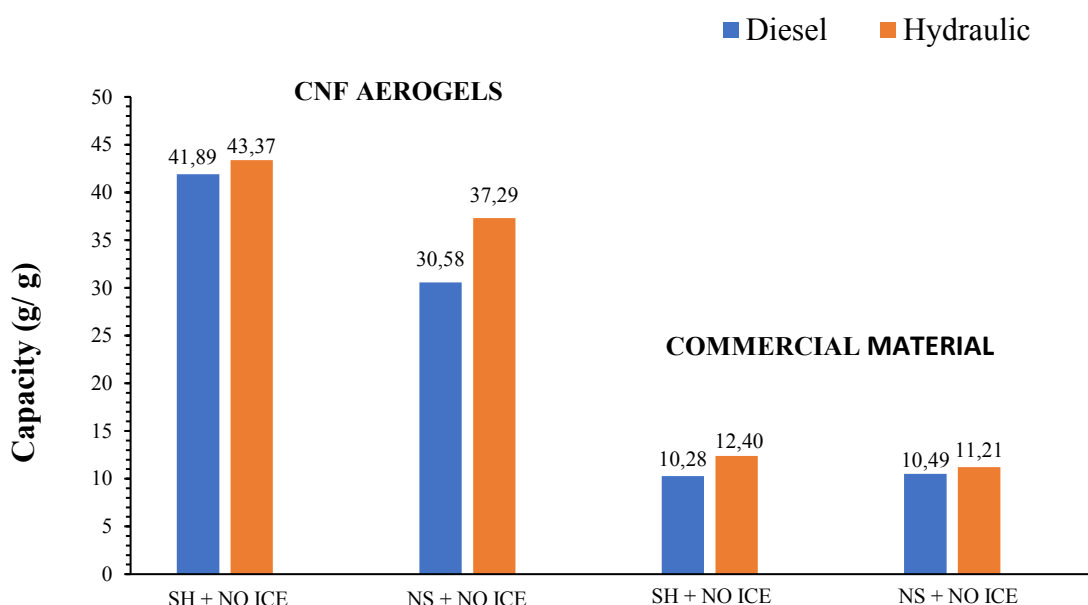


Figure 12. Comparison of absorption of diesel and hydraulic oil in 3.5% salinity. SH means shaking condition and NS means a no-shaking condition.

6.2.3 Comparison of the behaviour of hydraulic and diesel oils in different salinity

Figure 13 shows the behaviour of hydraulic oil in 1 and 3.5% salinity. In this comparison, hydraulic oil absorption (no-ice condition) with a pairwise combination of shaking and no-shaking conditions was considered in 1 and 3.5% salinity (Figure 11 and 12). From Figure 13, hydraulic oil had a notably higher absorption capacity in 3.5% salinity compared to 1% salinity. Generally, the highest absorption capacity for the CNF aerogel and commercial material were under shaking condition. This confirms that hydraulic oil absorption capacity is higher under shaking condition in 3.5 salinity.

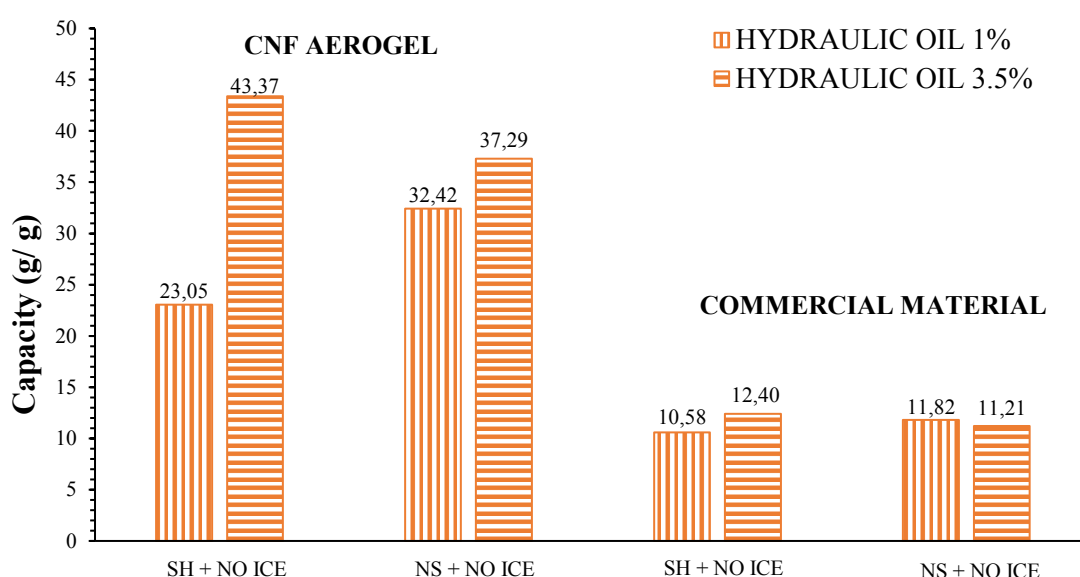


Figure 13. Effect of salinity on the hydraulic oil absorption. SH means shaking condition and NS means a no-shaking condition.

Figure 14 presents a dramatic effect of water salinity on diesel oil absorption. In this comparison, diesel oil absorption (no-ice condition) with a pairwise combination of shaking and no-shaking conditions was considered in 1 and 3.5% salinity (Figure 11 and 12). From Figure 14, it is evident that diesel oil recovery in 1% salinity was better than in 3.5 % salinity. No-shaking condition had the highest diesel oil absorption for both sorbent materials. This confirms what has already been stated that diesel oil has high absorption in no-shaking condition.

As Figures 13 and 14 have indicated, the salinity of the water had a major impact on the oil type removed. The lower the oil viscosity, the better the capacity in low salinity water

and the higher the oil viscosity, the excellent the absorption capacity in high salinity water.

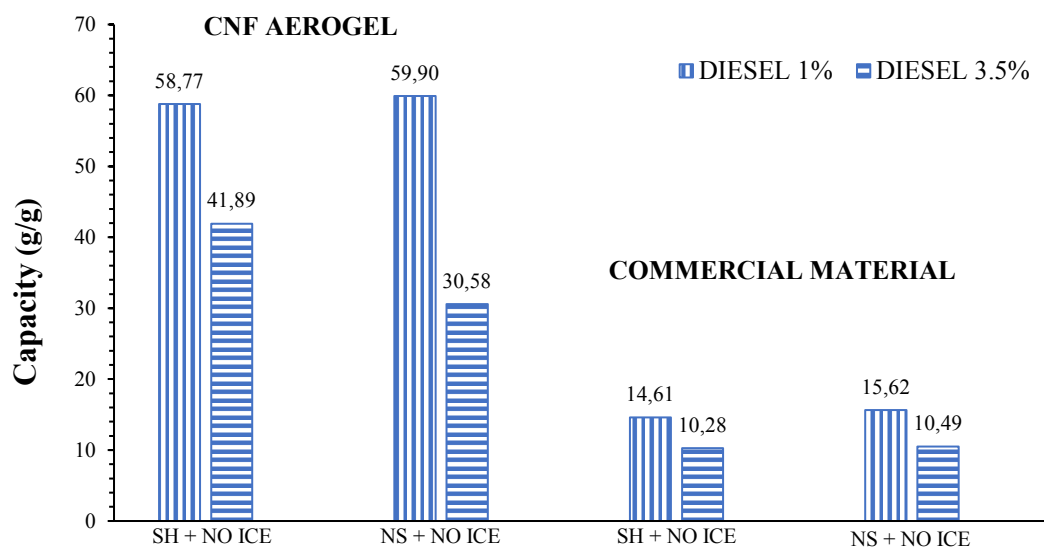


Figure 14. Effect of salinity on the diesel oil absorption. SH means shaking condition and NS means a no-shaking condition.

6.2.4 Effect of hydrodynamic conditions

Figures 15 and 16 presents the effect of shaking on the absorption capacity for oils (diesel and hydraulic) in 1 and 3.5% salinity. A shaking frequency of 100 rpm was constantly used in the experiments. To know the actual effect of shaking on the absorption capacity of oil, shaking in no-ice condition was considered (Tables 7 and 8). Generally, the shaking produced higher irregular fluctuations on the absorption capacity for the CNF aerogels. The fluctuations were high for the CNF aerogels in diesel oil absorption (1% salinity) (Figure 15) and CNF aerogels hydraulic oil absorption (1 and 3.5% salinity) (Figure 16). However, the shaking did not have effect on the maximum quantity of oil removed for both oils (diesel and hydraulic). The commercial materials in both salinities were less affected by the shaking condition for both oils' absorption capacity. In addition, the continues process of shaking caused the hydraulic oil to foam after 60 mins (not shown on the graph).

The reasons for the increasing and decreasing trends in absorption capacity was due to the oil type. Especially, the hydraulic oil drifted away from the sorbents (CNF aerogels and commercial material) towards the walls of the beaker (not shown on the graph). The

oil particles moved faster at 100 rpm and this caused less oil contact time with the absorbent, and, therefore, affected absorption capacity of the CNF aerogels. Some sources have confirmed that high shaking frequencies (72 rpm and above) affect the oil contact time and absorption capacity of absorbent materials (Zou et al. 2015; Abdelwahab et al. 2017).

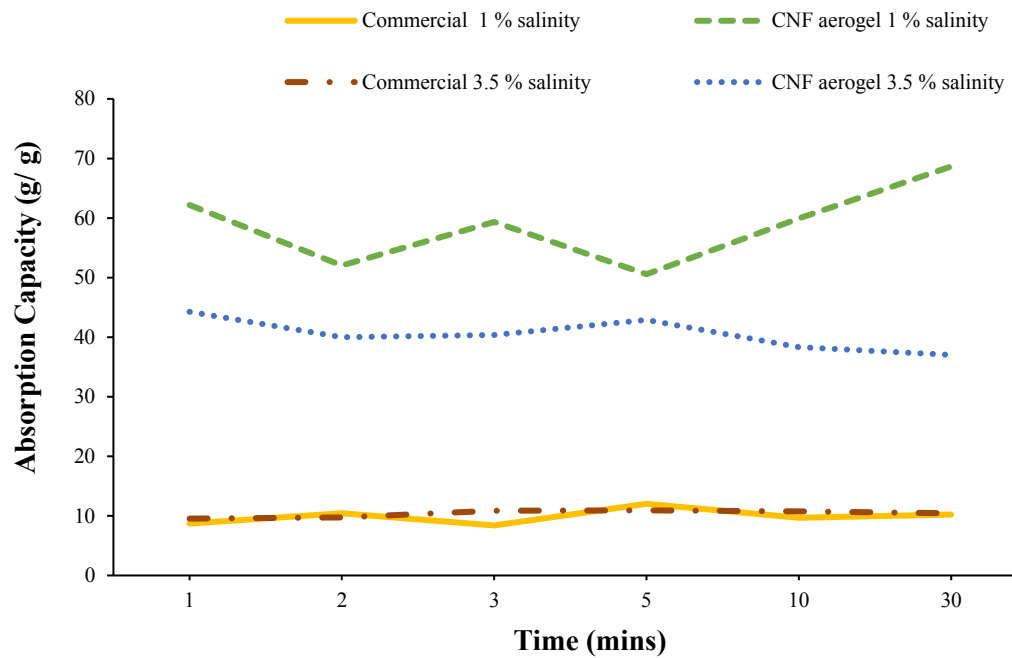


Figure 15. Effect of shaking on diesel oil absorption.

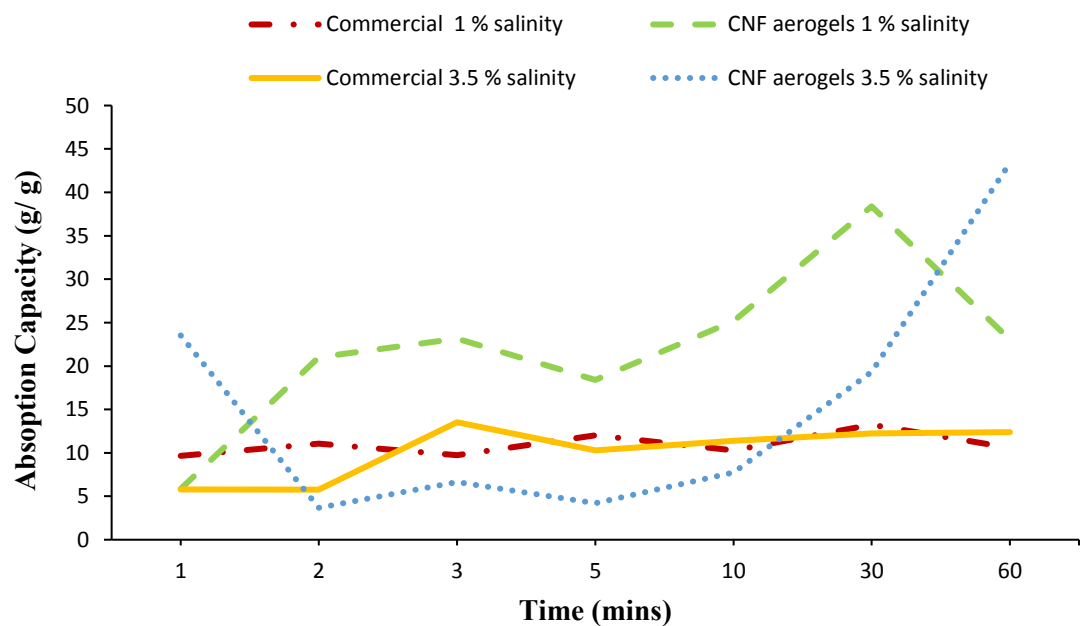


Figure 16. Effect of shaking on hydraulic oil absorption capacity.

In contrast, low shaking frequency (60 rpm and below) do not have effect on the maximum oil absorption capacity but rather decreases the required removal time (Zekri 2005). In addition, the huge shaking effect for the CNF aerogels could have been caused by their light weight. Overall, oil absorption capacity obtained under shaking condition for CNF aerogels in both salinities (Figures 15 and 16) were high.

The effect of no-shaking condition on diesel and hydraulic oil absorption are illustrated in Figures 17 and 18 under both 1 and 3.5% salinity. To know the actual effect of no-shaking on the absorption capacity of oil, no-shaking in no-ice condition was considered (Tables 7 and 8). Generally, oils (diesel and hydraulic) absorption capacity for CNF aerogels were largely affected under no-shaking condition (Figures 17 and 18) in both 1 and 3.5 % salinities. There was low effect on the commercial materials absorption. The hydraulic oil absorption for the CNF aerogels encountered the highest instability of oil absorption capacity in 1 and 3.5% salinity (Figure 18). The variations in absorption capacities were due to the lack of absorbent movement. This resulted in unsaturated pores within the CNF aerogels and commercial materials (not shown in the graph). Overall, oil absorption capacity obtained under no-shaking condition for CNF aerogels in both salinities (Figures 17 and 18) were low.

Moreover, there has not been enough research published on shaking and no-shaking effect under Arctic conditions and therefore, more studies are required to confirm the results.

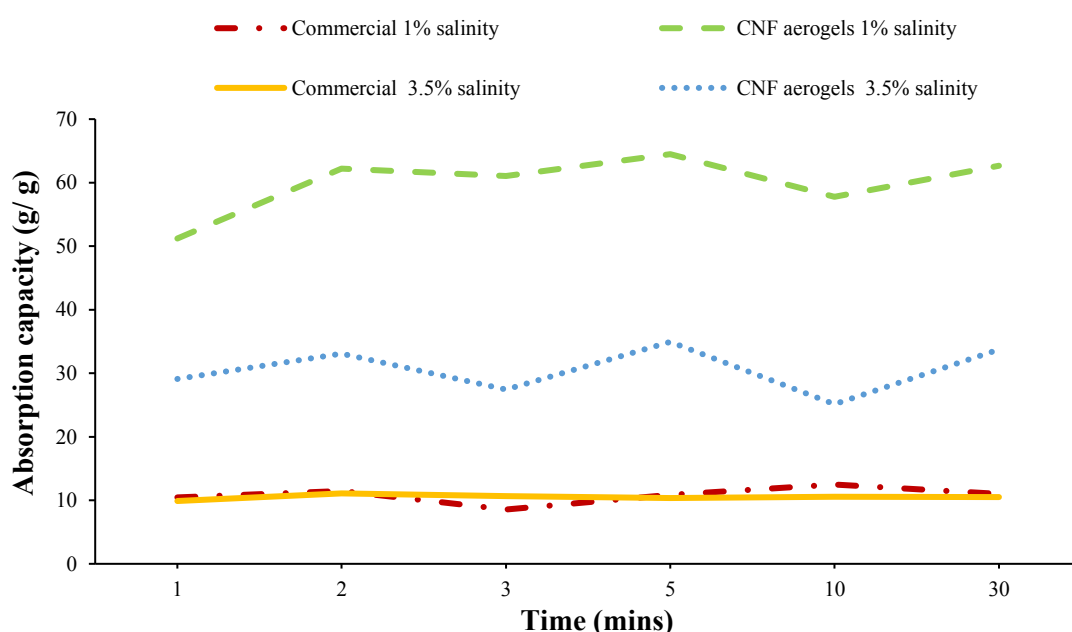


Figure 17. Effect of no-shaking on diesel oil absorption capacity.

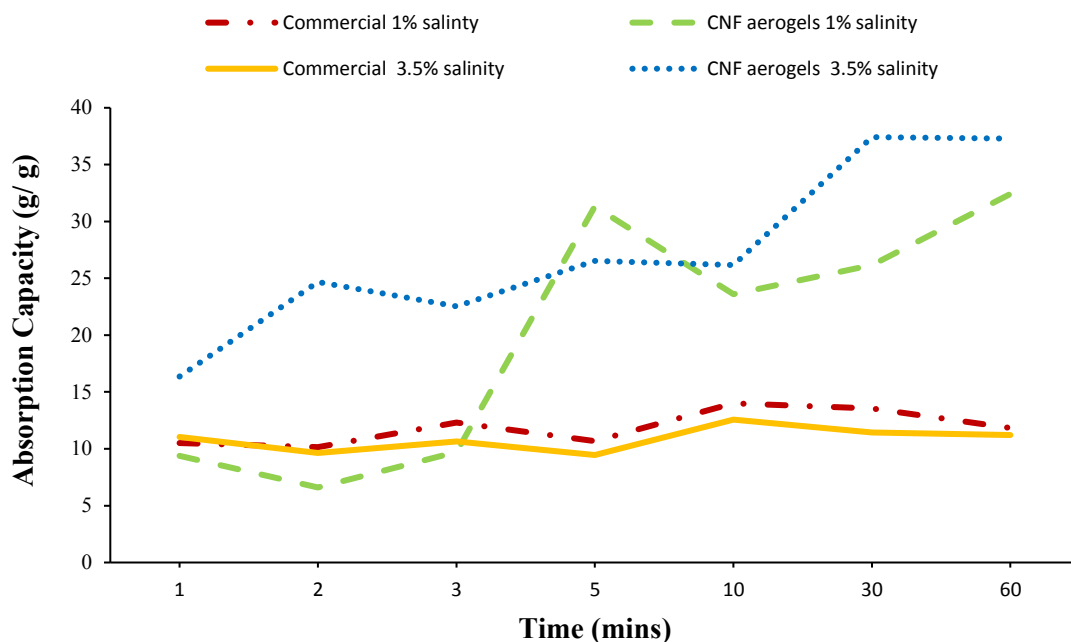


Figure 18. Effect of no-shaking on hydraulic oil absorption capacity.

6.2.5 Effect of ice on oil absorption

The effect of ice on the absorption capacity was experimentally investigated. Figures 19 and 20 shows that the presence of ice caused irregular increasing and decreasing absorption capacity. The effect was higher on the CNF aerogels capacity compared to the commercial reference materials. To know the actual effect of icy condition, no-shaking (with ice) model was considered in 1% salinity (Table 7). As shown in Figure 11, the CNF aerogels had lower diesel oil absorption in the icy condition (54.29 g/g) compared to no-ice condition (59.90 g/g) (Figure 11). The commercial material also had lower diesel oil absorption in icy condition (13.96 g/g) compared to no-ice condition (15.62 g/g) (Figure 11). This was same with hydraulic oil, where the CNF aerogels absorption capacity in icy condition (28.46 g/g) was lower compared to no-ice condition (32.42 g/g) Figure (11). Figure 21a and b illustrates that oils (diesel and hydraulic) and both absorbents were trapped by the ice cubes. In addition, the ice cubes acted as boom by holding the oil to be absorbed from spreading. This have been confirmed by some researchers as being a hindrance to oil removal capacity (Dickins et al. 2008; Lampela 2011; Scholz et al. 2012; Muizis 2013; Dickins 2017).

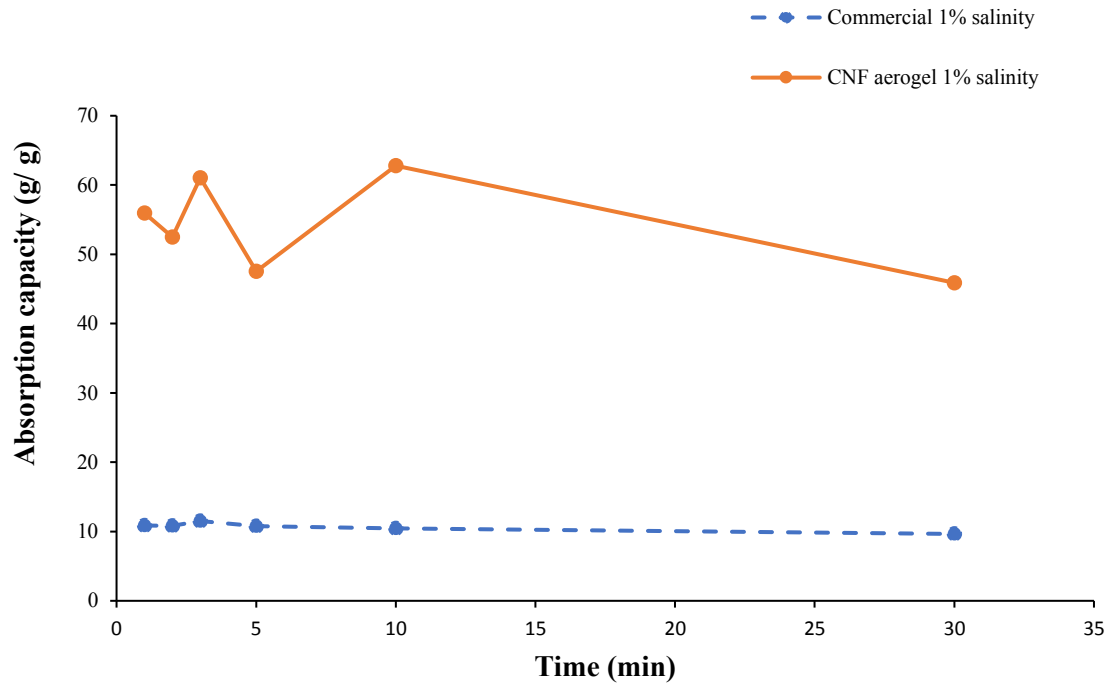


Figure 19. Effect of ice on absorption of oil diesel and absorbent.

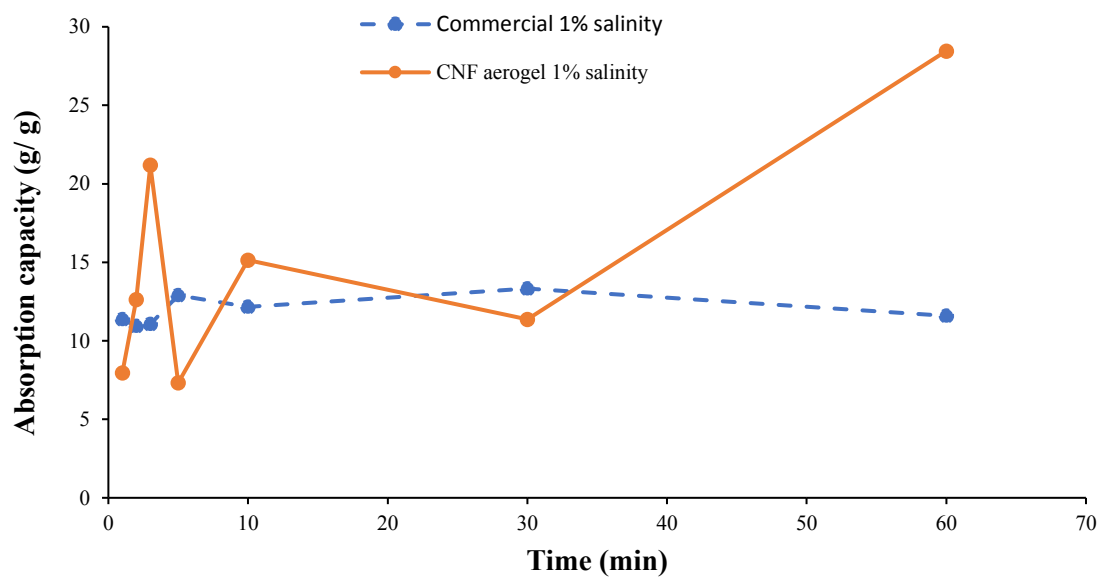


Figure 20. Effect of ice on hydraulic oil and absorbents absorption.

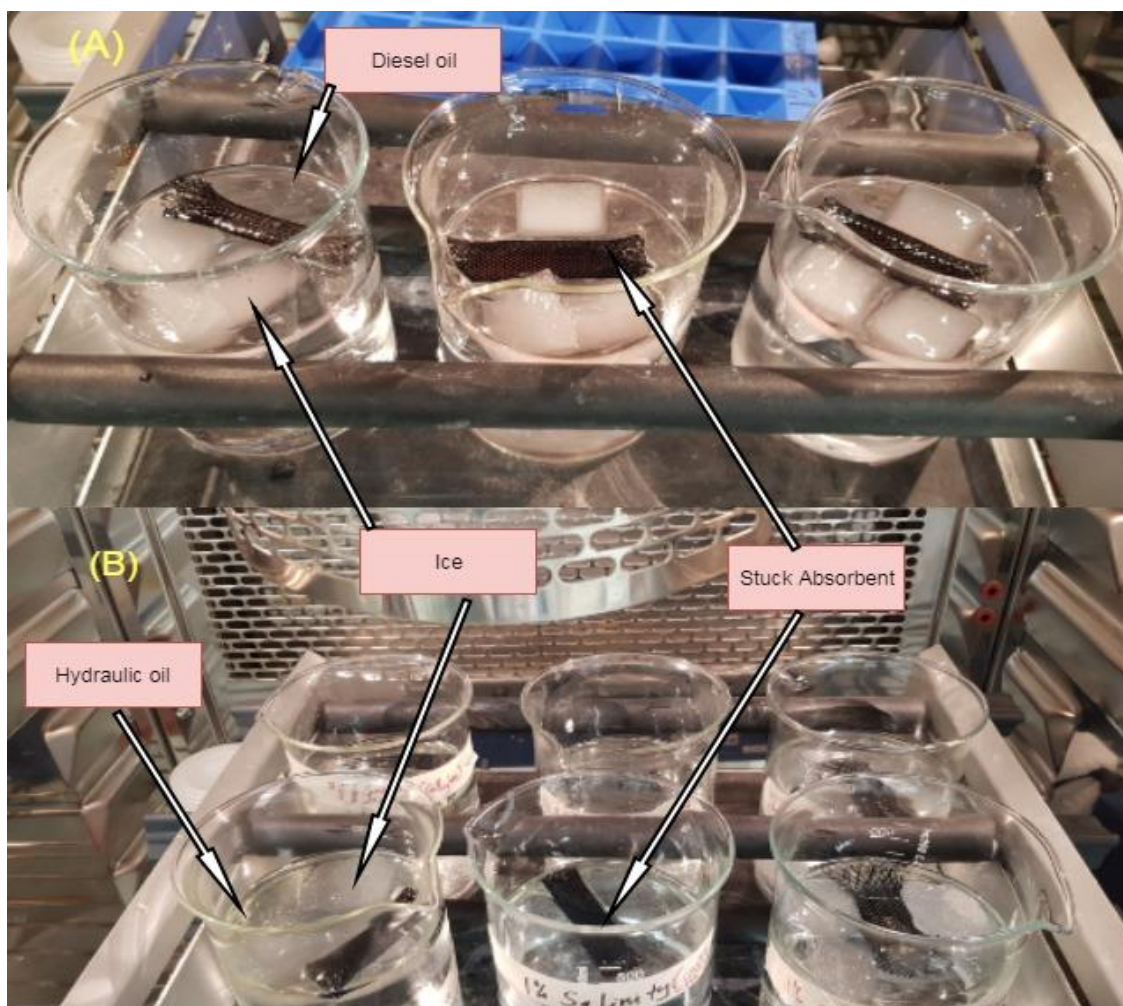


Figure 21. Effect of ice on oil and absorbents absorption.

6.2.6 Effect of temperature on oil absorption

The result of temperature at 0°C on the oils (hydraulic and diesel), and absorption capacity of CNF aerogels and commercial material were investigated. The coldness of the water reduced evaporation of the oils (diesel and hydraulic). The cold water made the hydraulic oil sticky (increased viscosity) and thick, and this caused the commercial material to be trapped on the ice cubes (not shown). Therefore, more energy would be required to absorb the oil. This has been already been confirmed by Lampela 2011 and Muizis 2013. In addition, the 0 °C temperature also reduced the random motion of the oil particles due to the increase in the viscosity of the oils. This could have made the oil penetration into the pores of absorbent difficult and might have caused decrease in oil absorption capacity. This has also been confirmed by Abdelwahab et al. 2017.

6.3 Limitations of the study

Despite the encouraging results obtained from the experiment, some challenges were also faced during the experiments. They include:

- The oils around the beaker wall were difficult to be absorbed especially under shaking condition.
- The shape of “mini booms” CNF aerogels (elongated shape) prevented them from absorbing oils close to the beaker wall.
- The low flexibility and fragile nature of cellulose sponges made it difficult to handle especially when inserting inside the sleeving material.
- Lack of space in the beaker resulted in non-movement of ice cubes

6.4 Recommendations for further research

To improve on the current study, the following changes are recommended;

- Nanocellulose aerogels should be prepared to have a circular shape that can cover a larger area of the surrounding oil slick.
- The use of a large conduit to provide enough space for oil and absorbent movement.
- We recommend the size of ice should be reduced by 1.5 cm in future studies to facilitate free flow of oil and absorbent.
- The time allocated for these experiments was not enough, therefore, a day should be enough for each experiment to enhance the weathering of oils and its effect on oil absorption.
- The use of different temperatures to see their effect on shaking condition and maximum absorption capacity.
- The use of different kinds of oils to determine the behaviour of CNF aerogels.
- Further developments of CNF aerogels are recommended to withstand hydrodynamic (wave) conditions.
- There are no designed and well-functioning models on how cellulose nanofibril aerogels can be of help to responders in connection of accidental oil releases in Arctic condition. Therefore, future models should be developed for such purpose.
- Further research work on this study should be conducted to optimise cellulose nanofibril aerogels beyond the Arctic region for oil spill response. The research

should be a pragmatic option that will deal with, for example, other marine conditions and environments.

7 SUMMARY AND CONCLUSIONS

Oil spills have generally been recognised as serious concerns by industries, NGOs and governments due to their impact on the environment and human health. Oil spill in the Arctic is a risk, presenting itself hazard to the Arctic marine environment and coastal regions. Oil spill remains a key pollutant from Arctic port activities causing various forms of pollution within the port, at sea and shore land areas. The aim of this thesis was to address shoreline oil spill clean-up at Arctic harbours (Oulu and Tromsø). The focus was on the application of sorbents (cellulose nanofibril aerogels (CNFs) oil sorbent) in the oil spill clean-up. Sorbents serve as a suitable resource for oil spill response, which recovers oil in a way that is difficult for other technologies. Nanofibril aerogel oil sorbents have high recovery and removal efficiency and ultrahigh absorption capacity. They are widely available, cost-effective and safe, renewable, good mechanical properties, low density, high porosity, natural biodegradability and environmentally friendly. Nanofibril aerogel are obtained from renewable resources and its environmentally friendly manufacturing process makes it a very good alternative for oil removal in the Arctic marine environment.

In this thesis an ultralow density (0.01 g/cm^3), high porous (99.15%), reusable, cost-effective nanofibril aerogel was produced from recycled fibre. A simple but environmentally friendly nanofibrillation treatment, which involved drying-freezing and, the combination of two silylation agents were used for the fabrication of the cellulose nanofibril aerogel oil sorbents (CNFs). An experiment was performed by simulating winter sea conditions in the laboratory. A climate chamber served as an artificial Arctic environment simulator. The Arctic conditions (ice, salinity (1 and 3.5%), shaking and no-shaking and temperature), all together created winter sea conditions in the experiment.

For the first time, CNF aerogels have been used to absorb oil in a simulated Arctic marine condition. Coating the material with silylated agents made it more hydrophobic and oleophilic. The CNF aerogel showed higher oil absorption capacity in both 1 and 3.5% salinity water over the commercial (polypropylene) absorbent. The CNF aerogel showed stronger affinities to both diesel and hydraulic oil. The prepared CNF aerogels had a low density and a higher porosity compared to the commercial materials.

It was found that in 1 and 3.5% salinity, both shaking, and no-shaking conditions caused high fluctuations in the oil (diesel and hydraulic) absorption capacity for the CNF aerogel compared to those of commercial absorbent (polypropylene). The shaking condition reduced the oil contact time with CNF aerogels but this did not influence maximum

absorption capacity. No-shaking condition reduced oil absorption within the pores of the CNF aerogel and affected maximum oil absorption capacity. The low density and weight contributed to the high shaking condition effect on the CNF aerogels. Icy condition decreased absorption capacity for both oil with CNF aerogel and commercial material. Ice effect was high on the CNF aerogels compared to the commercial materials.

The diesel oil had higher absorption in 1% salinity water whiles hydraulic oil absorption was high in 3.5% salinity water. The absorption rate of diesel oil was faster compared to the hydraulic oil under all conditions. The cold temperature affected oil evaporation, and made the hydraulic oil sticky and thick.

The following conclusions can be drawn from the results obtained from the present study

- In general, the success of removing (maximum percentage of oil) depends on the combined effect of shaking and no-shaking conditions, surface properties, oil type, slick thickness, temperature, ice and salinity. All the above affect oil absorption capacity.
- It is possible to clean oil spills with our prepared hydrophobicized cellulose nanofibril aerogels. This could be one of the most promising absorbents for oil spill removal in the Arctic.
- CNF aerogels have demonstrated that high oil absorption capacity can be obtained in Arctic marine condition than those of the commercial reference materials.
- Oil removal for low density oil (diesel) are better in low salinity water. In contrast, high density oil (hydraulic) are better absorbed in high salinity water.
- The higher the oils viscosity, the lower its absorption in brackish water, and the lower the oils viscosity, the lower its absorption in a high salinity water.

Finally, this study concluded that superabsorbent CNF aerogels are a sustainable solution for oil spill response in Arctic marine conditions.

8 REFERENCES

- Abdelwahab, O., Nasr, S. M., and Thabet, W. M., 2017. Palm fibers and modified palm fibers adsorbents for different oils. *Alexandria Engineering Journal*, 56 (4), 749–755.
- Adebajo, M. O., Frost, R. L., Klopogge, J. T., Carmody, O., and Kokot, S., 2003. Porous Materials for Oil Spill Cleanup: A Review of Synthesis and Absorbing Properties. *Journal of Porous Materials*, 10, 159–170.
- Aljammal, N. and Juzsakova, T., 2016. Review on the Effectiveness of Adsorbent Materials in Oil Spills, (October), 9.
- Angelova, D., Uzunov, I., Uzunova, S., Gigova, A., and Minchev, L., 2011. Kinetics of oil and oil products adsorption by carbonized rice husks. *Chemical Engineering Journal*, 172, 306–311.
- Annunciado, T. R., Sydenstricker, T. H. D., and Amico, S. C., 2005. Experimental investigation of various vegetable fibers as sorbent materials for oil spills, 50, 1340–1346.
- ART, 2015. Mechanical recovery in ice -Summary Report [online]. Available from: <http://www.arcticresponsetechnology.org/>.
- ATSDR, 1995. Chemical and physical information of oil. [online]. Atlanta, Georgia. Available from: <https://www.atsdr.cdc.gov/toxprofiles/tp75-c3.pdf> [Accessed 4 Apr 2019].
- Babel, S. and Kurniawan, T. A., 2010. CAB Direct. *African Journal of Range & Forage Science*, 22 (1), 73–74.
- Bandura, L., Franus, M., Józefaciuk, G., and Franus, W., 2015. Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup. *Fuel*, 147, 100–107.
- Bayat, A., Aghamiri, S. F., Moheb, A., and Vakili-Nezhaad, G. R., 2005. Oil spill cleanup from sea water by sorbent materials. *Chemical Engineering and Technology*, 28 (12), 1525–1528.
- Bi, H., Xie, X., Yin, K., Zhou, Y., Wan, S., He, L., Xu, F., Banhart, F., Sun, L., and Ruoff, R. S., 2012. Spongy graphene as a highly efficient and recyclable sorbent for oils and organic solvents. *Advanced Functional Materials*, 22 (21), 4421–4425.
- Blindheim, J., 2004. Oceanography and climate. In: Skjoldal, H.R. (Ed.), *The Norwegian Sea Ecosystem*. Tapir Academic Press, Trondheim, pp. 65–96.
- Board, O. S., Studies, L., and Board, M., 2014. Responding to Oil Spills in the U.S. Arctic Marine Environment. In: [online]. Washington DC: The national Academy Press, 211. Available from: <http://www.nap.edu/catalog/18625>.
- Bobra, A. M. and Fingas, M. F., 1986. The Behaviour and Fate of Arctic Oil Spills. *Water Science and Technology*, 18 (2), 13–23.
- Brakstad, O. G., Throne-Holst, M., Netzer, R., Stoeckel, D. M., and Atlas, R. M., 2015. Microbial communities related to biodegradation of dispersed Macondo oil at low seawater temperature with Norwegian coastal seawater. *Microbial Biotechnology*, 8 (6), 989–998.

- Buist, I., Belore, R., Dickins, D., Hackenberg, D., Guarino, A., and Zhendi, W., 2008. Empirical Weathering Properties of Oil in Ice and Snow. *Science And Technology*, (1435), 154.
- Cai, J., Kimura, S., Wada, M., Kuga, S., and Zhang, L., 2008. Cellulose Aerogels from Aqueous Alkali Hydroxide–Urea Solution. *ChemSusChem*, 1 (1–2), 149–154.
- Cai, J., Liu, S., Feng, J., Kimura, S., Wada, M., Kuga, S., and Zhang, L., 2012. Cellulose-silica nanocomposite aerogels by in-situ formation of silica in cellulose gel. *Angewandte Chemie - International Edition*, 51 (9), 2076–2079.
- Cervin, N. T., Aulin, C., Larsson, P. T., and Wågberg, L., 2012. Ultra porous nanocellulose aerogels as separation medium for mixtures of oil/water liquids. *Cellulose*, 19 (2), 401–410.
- Choi, H. and Cloud, R. M., 1992. Natural Sorbents in Oil Spill Cleanup. *Environmental Science and Technology*, 26 (4), 772–776.
- Daling, P. S. and Strøm, T., 1999. Weathering of oils at sea: Model/field data comparisons. *Spill Science and Technology Bulletin*, 5 (1), 63–74.
- Deschamps, G., Caruel, H., Borredon, M. E., Bonnin, C., and Vignoles, C., 2003. Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. *Environmental Science and Technology*, 37 (5), 1013–1015.
- Dickins, D., Brandvik, P. J., Bradford, J., Faksness, L.-G., Liberty, L., and Daniloff, R., 2008. Experimental oil spill under ice: remote sensing, oil weathering under arctic conditions and assessment of oil removal by in-situ burning. *International Oil Spill Conference Proceedings*, (1), 681–688.
- Dickins, D. F., 2017. Arctic oil spill response technology joint industry programme synthesis report. Arctic Response Technology JIP [online]. California. Available from: <http://www.arcticresponsetechnology.org/news/arctic-oil-spill-response-technology-jip-synthesis-report>.
- Doshi, B., Sillanpää, M., and Kalliola, S., 2018. A review of bio-based materials for oil spill treatment. *Water Research*, 135, 262–277.
- Dufresne, A., 2013. Nanocellulose: A new ageless bionanomaterial. *Materials Today*, 16 (6), 220–227.
- Dumitriu, S., 1996. Polysaccharides in medicinal applications [online]. New York: M. Dekker, Inc. Available from: www.crcpress.com/Polysaccharides-in-Medicinal-Applications/Dumitriu/p/book/9780824795405.
- Dutta, T. . and Harayama, S., 2000. Fate of Crude Oil by the Combination of Photooxidation and Biodegradation. *Environmental Science and Technology*, 34, 6.
- EEA, 2009. Arctic Ocean physiography (depth distribution and main currents in the European part) [online]. Available from: <https://www.eea.europa.eu/data-and-maps/figures/arctic-ocean-physiography-depth-distribution-and-main-currents-in-the-european-part> [Accessed 7 May 2019].
- EPPR, 2017. Circumpolar oil spill response viability analysis: Technical Report [online]. Washington, DC. Available from: <https://oaarchive.arctic-council.org/handle/11374/2100>.

- Eyu, G. D., Mansor, A. M., Ahmad, Z., Chukwuekezie, C. S., and Idris, J., 2014. A Preliminary Study of Biodegradable Waste as Sorbent Material for Oil-Spill Cleanup. *The Scientific World Journal*, 2014, 1–5.
- Faksness, L. G., Brandvik, P. J., Daae, R. L., Leirvik, F., and Børseth, J. F., 2011. Large-scale oil-in-ice experiment in the Barents Sea: Monitoring of oil in water and MetOcean interactions. *Marine Pollution Bulletin*, 62 (5), 976–984.
- Federici, C., Mintz, J., Teas, C., Kalligeros, S., Zankos, F., Stoumas, S., Lois, E., and Anastopoulos, G., 2014. Oil Properties and Their Impact on Spill Response Options Literature Review. *CNA Analysis & Solutions*, 140 (1), 1–92.
- Feng, J., Nguyen, S. T., Fan, Z., and Duong, H. M., 2015. Advanced fabrication and oil absorption properties of super-hydrophobic recycled cellulose aerogels. *Chemical Engineering Journal*, 270, 168–175.
- Fingas, M. and Brown, C., 2001. <A-Review-of-the-Status-of-Advanced-Technologies-for_2000_Spill-Science---Tec.pdf>, 6 (5), 295–302.
- Fingas, M. F., 2011. Review of Solidifiers, (12), 1156.
- Fingas, M. F., 2015. Handbook of oil spill science and technology [online]. Hoboken, NJ: John Wiley & Sons, Inc. Available from: <http://doi.wiley.com/10.1002/9781118989982> [Accessed 4 Apr 2019].
- Fischer, F., Rigacci, A., Pirard, R., Berthon-Fabry, S., and Achard, P., 2006. Cellulose-based aerogels. *Polymer*, 47 (22), 7636–7645.
- Fu, R., Zheng, B., Liu, J., Dresselhaus, M. S., Dresselhaus, G., Satcher, J. H., and Baumann, T. F., 2003. The Fabrication and Characterization of Carbon Aerogels by Gelation and Supercritical Drying in Isopropanol. *Advanced Functional Materials*, 13 (7), 558–562.
- Fumagalli, M., Ouhab, D., Boisseau, S. M., and Heux, L., 2013. Versatile gas-phase reactions for surface to bulk esterification of cellulose microfibrils aerogels. *Biomacromolecules*, 14 (9), 3246–3255.
- Gavillon, R. and Budtova, T., 2008. Aerocellulose: New Highly Porous Cellulose Prepared from Cellulose–NaOH Aqueous Solutions. *Biomacromolecules*, 9 (1), 269–277.
- Ghaly, A. E. and Dave, D., 2011. Remediation Technologies for Marine Oil Spills: A Critical Review and Comparative Analysis. *American Journal of Environmental Sciences*, 7 (5), 423–440.
- Glickson, D., Grabowski, M., Coolbaugh, T., Dickins, D., Glenn, R., Lee, K., Majors, L., Myers, M., Norcross, B., Reed, M., Suydam, R., Tiedje, J., Timmermans, M.-L., and Wadhams, P., 2014. Responding to Oil Spills in the U.S. Arctic Marine Environment. *International Oil Spill Conference Proceedings*, 2014 (1), 283740.
- Groll, N., Grabemann, I., Hünicke, B., and Meese, M., 2017. Baltic sea wave conditions under climate change scenarios. *Boreal Environment Research*, 22, 1–12.
- Gu, J., Xiao, P., Chen, J., Zhang, J., Huang, Y., and Chen, T., 2014. Janus polymer/carbon nanotube hybrid membranes for oil/water separation. *ACS Applied Materials and Interfaces*, 6 (18), 16204–16209.

- Gui, X., Li, H., Wang, K., Wei, J., Jia, Y., Li, Z., Fan, L., Cao, A., Zhu, H., and Wu, D., 2011. Recyclable carbon nanotube sponges for oil absorption. *Acta Materialia*, 59 (12), 4798–4804.
- Gui, X., Zeng, Z., Lin, Z., Gan, Q., Xiang, R., Zhu, Y., Cao, A., and Tang, Z., 2013. Magnetic and highly recyclable macroporous carbon nanotubes for spilled oil sorption and separation. *ACS Applied Materials and Interfaces*, 5 (12), 5845–5850.
- Gupta, S. and Tai, N.-H., 2016. Carbon materials as oil sorbents: a review on the synthesis and performance, 1–16.
- Gurung, M., Adhikari, B. B., Gao, X., Alam, S., and Inoue, K., 2014. Sustainability in the metallurgical industry: Chemically modified cellulose for selective biosorption of gold from mixtures of base metals in chloride media. *Industrial and Engineering Chemistry Research*, 53 (20), 8565–8576.
- Hazen, T. C., Dubinsky, E. A., DeSantis, T. Z., Andersen, G. L., Piceno, Y. M., Singh, N., Jansson, J. K., Probst, A., Borglin, S. E., Fortney, J. L., Stringfellow, W. T., Bill, M., Conrad, M. E., Tom, L. M., Chavarria, K. L., Alusi, T. R., Lamendella, R., Joyner, D. C., Spier, C., Baelum, J., Auer, M., Zemla, M. L., Chakraborty, R., Sonnenthal, E. L., D'haeseleer, P., Holman, H.-Y. N., Osman, S., Lu, Z., Van Nostrand, J. D., Deng, Y., Zhou, J., and Mason, O. U., 2010. Deep-sea oil plume enriches indigenous oil-degrading bacteria. *Science (New York, N.Y.)*, 330 (6001), 204–8.
- HELCOM, 2009. Helsinki Commission Baltic Marine Environment Protection Commission HELCOM Ensuring safe shipping in the Baltic HELCOM, ensuring safe shipping in the Baltic [online]. Helsinki. Available from: www.helcom.fi [Accessed 22 Jan 2019].
- HELCOM, 2018. Baltic Marine Environment Protection Commission Baltic Sea Environment Proceedings 155 Baltic Sea-Second HELCOM holistic [online]. Available from: www.helcom.fi/baltic-sea-trends/holistic-assessments/state-of-the-baltic-sea-2018/reports-and-materials/ [Accessed 17 Jan 2019].
- Hokkanen, S., Bhatnagar, A., and Sillanpää, M., 2016. A review on modification methods to cellulose-based adsorbents to improve adsorption capacity. *Water Research*, 91, 156–173.
- Holakoo, L., 2001. On the capability of Rhamnolipids for oil spill control of surface water. [online]. Concordia University, Montreal, Quebec, Canada. Available from: <https://spectrum.library.concordia.ca/1745/>.
- Hossain, T. M., 2018. Assessment of sustainability initiatives in port operations: an overview of global and canadian ports. Dalhousie University.
- Hurrell, J. W., 1995. Decadal Trends in the North Atlantic Oscillation: Regional Temperatures and Precipitation, 269 (August), 676–679.
- ICES, 2008. 3 The Barents Sea and the Norwegian Sea 3.1 Ecosystem Overview 3.1.1 Ecosystem components [online]. Available from: [http://www.ices.dk/sites/pub/Publication Reports/Advice/2008/2008/3.1-3.2 Barents Sea Ecosystem Overview.pdf](http://www.ices.dk/sites/pub/Publication%20Reports/Advice/2008/2008/3.1-3.2%20Barents%20Sea%20Ecosystem%20Overview.pdf) [Accessed 22 Jan 2019].
- Innerlohinger, J., Weber, H. K., and Kraft, G., 2006. Aerocellulose: Aerogels and aerogel-like materials made from cellulose. *Macromolecular Symposia*, 244, 126–135.

- ITOPF, 2011. Fate of marine oil spill. [online], 1–12. Available from: www.itopf.com.
- ITOPF, 2012a. TIP 08: Use of sorbent materials in oil spill response. ITOPF Technical Information Paper [online], 12. Available from: <https://www.itopf.org/knowledge-resources/documents-guides/technical-information-papers/>.
- ITOPF, 2012b. TIP 17: Response To Marine Chemical Incidents. ITOPF Technical Information Paper [online], 17. Available from: <https://www.itopf.org/knowledge-resources/documents-guides/technical-information-papers/>.
- ITOPF, 2014. Use of Booms in Oil Pollution Response [online]. Technical Information Paper. Available from: <https://www.itopf.org/knowledge-resources/documents-guides/document/tip-03-use-of-booms-in-oil-pollution-response/>.
- Jiang, F. and Hsieh, Y. L., 2014. Amphiphilic superabsorbent cellulose nanofibril aerogels. *Journal of Materials Chemistry A*, 2 (18), 6337–6342.
- Jin, H., Nishiyama, Y., Wada, M., and Kuga, S., 2004. Nanofibrillar cellulose aerogels. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 240 (1–3), 63–67.
- Jokuty, P., Whiticar, S., Fingas, M., Meyer, E., and Knobel, C., 1995. Hydrocarbon Groups and Their Relationships to Oil Properties and Behaviour. In: Whiticar Scientific. Ottawa, 1–20.
- Karana, C. P., Rengasamy, R. S., and Das, D., 2011. Oil spill cleanup by structured fibre assembly. *Indian Journal of Fibre and Textile Research*, 36 (2), 190–200.
- Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A., 2005. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. *Angewandte Chemie International Edition*, 44 (22), 3358–3393.
- Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., and Dorris, A., 2011. Nanocelluloses: A new family of nature-based materials. *Angewandte Chemie - International Edition*, 50 (24), 5438–5466.
- Klemm, D., Philpp, B., Heinze, T., Hewinze, U., and Wagenknecht, W., 1998. Comprehensive cellulose chemistry. Volume 2: Functionalization of cellulose. *Comprehensive cellulose chemistry. Volume 2: Functionalization of cellulose.*, Volume 1, 1–33.
- Kobayashi, Y., Saito, T., and Isogai, A., 2014. Aerogels with 3D ordered nanofiber skeletons of liquid-crystalline nanocellulose derivatives as tough and transparent insulators. *Angewandte Chemie (International ed. in English)*, 53 (39), 10394–10397.
- Korhonen, J. T., Kettunen, M., Ras, R. H. A., and Ikkala, O., 2011. Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents. *ACS Applied Materials and Interfaces*, 3 (6), 1813–1816.
- Kyzas, G. Z. and Kostoglou, M., 2014. Green adsorbents for wastewaters: A critical review. *Materials*, 7 (1), 333–364.
- Laitinen, O., Suopajarvi, T., Österberg, M., and Liimatainen, H., 2017. Hydrophobic, Superabsorbing Aerogels from Choline Chloride-Based Deep Eutectic Solvent Pretreated and Silylated Cellulose Nanofibrils for Selective Oil Removal. *ACS Applied Materials and Interfaces*, 9 (29), 25029–25037.

- Lam, J. S. L. and Notteboom, T., 2014. The Greening of Ports: A Comparison of Port Management Tools Used by Leading Ports in Asia and Europe. *Transport Reviews*, 34 (2), 169–189.
- Lampela, K., 2011. Oil Spill Response in Finland [online]. Helsinki. Available from: <https://www.ymparisto.fi/download/noname/%7B75F2BD97-E343-4B87.../59271%0A>.
- Lee, K., Li, Z., Robinson, B., Kepkay, P. E., Blouin, M., and Doyon, B., 2011. Field Trials of in-situ Oil Spill Countermeasures in Ice-Infested Waters. *International Oil Spill Conference Proceedings*, 2011 (1), abs160.
- Li, P., Cai, Q., Lin, W., Chen, B., and Zhang, B., 2016. Offshore oil spill response practices and emerging challenges. *Marine Pollution Bulletin*, 110 (1), 6–27.
- Lim, T. T. and Huang, X., 2006. In situ oil/water separation using hydrophobic-oleophilic fibrous wall: A lab-scale feasibility study for groundwater cleanup. *Journal of Hazardous Materials*, 137 (2), 820–826.
- Lin, C., Hong, Y. J., and Hu, A. H., 2010. Using a composite material containing waste tire powder and polypropylene fiber cut end to recover spilled oil. *Waste Management*, 30 (2), 263–267.
- Lindström, T.; Winter, L. Mikrofibrillär cellulosa som komponent vid papperstillverkning. Internal STFI report C159, 1988.
- Liu, H., Geng, B., Chen, Y., and Wang, H., 2017. Review on the Aerogel-Type Oil Sorbents Derived from Nanocellulose. *ACS Sustainable Chemistry and Engineering*, 5 (1), 49–66.
- Loeng, H. and Drinkwater, K., 2007. An overview of the ecosystems of the Barents and Norwegian Seas and their response to climate variability, 54, 2478–2500.
- Mahfoudhi, N. and Boufi, S., 2017. Nanocellulose as a novel nanostructured adsorbent for environmental remediation: a review. *Cellulose*, 24 (3), 1171–1197.
- Manning, F. S. and Thompson, R. E., 1995. Oilfield processing of petroleum [online]. Volume 2. Tulsa, Oklahoma: PennWell Publication Company. Available from: https://books.google.fi/books?id=BZOPIA-SmMUC&pg=PA21&dq=crude+oil+define&hl=ru&sa=X&ei=qrx6UeDcGYOO4ASTtoEY&redir_esc=y#v=onepage&q=crude oil define&f=false [Accessed 4 Apr 2019].
- Mapelli, F., Scoma, A., Michoud, G., Aulenta, F., Boon, N., Borin, S., Kalogerakis, N., and Daffonchio, D., 2017. Biotechnologies for Marine Oil Spill Cleanup: Indissoluble Ties with Microorganisms. *Trends in Biotechnology*, 35 (9), 860–870.
- Margesin, R. and Schinner, F., 2001. Biodegradation and bioremediation of hydrocarbons in extreme environments. *Applied Microbiology and Biotechnology*, 56 (5–6), 650–663.
- McFarlin, K., Leigh, M. B., and Perkins, R., 2011a. Indigenous Microorganisms Degrade Oil in Arctic Seawater. *International Oil Spill Conference Proceedings*, (1), 132.

- McFarlin, K., Perkins, R., Gardiner, G., and Word, J. D., 2011b. Evaluating the biodegradability and effects of dispersed oil using arctic test species and conditions: Phase 2 activities. In Proceedings of the 34th Arctic and Marine Oilspill Program (AMOP) Technical Seminar on Environmental Contamination and Response. In: osti.gov. 4–6.
- Meier, H. E. M., 2006. Baltic Sea climate in the late twenty-first century: a dynamical downscaling approach using two global models and two emission scenarios, (11 April 2006), 1–30.
- Meng, Y., Young, T. M., Liu, P., Contescu, C. I., Huang, B., and Wang, S., 2015. Ultralight carbon aerogel from nanocellulose as a highly selective oil absorption material. *Cellulose*, 22 (1), 435–447.
- Moon, R. J., Martini, A., Nairn, J., Simonsen, J., and Youngblood, J., 2011. Cellulose nanomaterials review: structure, properties and nanocomposites. *Chemical Society Reviews*, 40 (7), 3941.
- Muizis, A., 2013. Evaluation of the Methods for the Oil Spill Response in the Offshore Arctic Region. [online]. Helsinki Metropolia University of Applied Sciences. Available from: <https://www.theseus.fi/bitstream/handle/10024/62953/AnnaMui1.pdf?sequence=1&isAllowed=y>.
- Mulyadi, A., Zhang, Z., and Deng, Y., 2016. Fluorine-Free Oil Absorbents Made from Cellulose Nanofibril Aerogels. *ACS Applied Materials & Interfaces*, 8 (4), 2732–2740.
- Nakagaito, A., Kondo, H., and Takagi, H., 2013. Cellulose nanofiber aerogel production and applications. *Journal of Reinforced Plastics and Composites*, 32 (20), 1547–1552.
- NASEM, 2016. Spills of Diluted Bitumen from Pipelines: A Comparative Study of Environmental Fate, Effects, and Response [online]. Washington, DC: The National Academies Press. Available from: <https://www.nap.edu/read/21834/chapter/10#128>.
- Ngah, W. S. and Hanafiah, M. A. K. M., 2008. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, 99 (10), 3935–3948.
- Nguyen, D. D., Tai, N. H., Lee, S. B., and Kuo, W. S., 2012. Superhydrophobic and superoleophilic properties of graphene-based sponges fabricated using a facile dip coating method. *Energy and Environmental Science*, 5 (7), 7908–7912.
- Nguyen, S. T., Feng, J., Kai Ng, S., Wong, J. P., Tan, V. B., and Duong, H. M., 2014. Advanced thermal insulation and absorption properties of recycled cellulose aerogels. *Physicochem. Eng. Aspects*, 445, 128–134.
- Nguyen, S. T., Feng, J., Le, N. T., Le, A. T. T., Hoang, N., Tan, V. B. C., and Duong, H. M., 2013. Cellulose aerogel from paper waste for crude oil spill cleaning. *Industrial and Engineering Chemistry Research*, 52 (51), 18386–18391.
- Niu, H., Lee, K., Boufadel, M. C., Zhao, L., and Robinson, B., 2014. In Situ Oil Spill Countermeasures in Ice-Infested Waters: A Modeling Study of the Fate/Behaviours of Spilled Oil. *International Oil Spill Conference Proceedings*, 2014 (1), 1215–1225.

- Njobuenwu, D. O. and Abowei, M. F. N., 2008. Spreading of Oil Spill on Placid Aquatic Medium on Leonardo J. Sci. Leonardo Journal of Sciences, (12), 11–24.
- Nordvik, A. B., Simmons, J. L., Bitting, K. R., Lewis, A., and Strom-Kristiansen, T., 1996. Oil and Water Separation in Marine Oil Spill Clean-up Operations. *Spill Science & Technology Bulletin*, 3 (3), 107–122.
- NRC, 2003. Oil in the Sea III: Oil in the Sea III: Inputs, Fates, and Effects [online]. 3rd ed. Washington, DC: The National Academies Press. Available from: <https://www.nap.edu/catalog/10388>.
- O’Connell, D. W., Birkinshaw, C., and O’Dwyer, T. F., 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology*, 99 (15), 6709–6724.
- OECD, 2011. Environmental Impacts of International Shipping [online]. Paris: OECD. Available from: https://www.oecd-ilibrary.org/environment/environmental-impacts-of-international-shipping_9789264097339-en.
- Olah, G. A. and Molnár, A., 2003. Hydrocarbon chemistry [online]. Available from: <https://www.wiley.com/en-us/Hydrocarbon+Chemistry%2C+2nd+Edition-p-9780471417828> [Accessed 4 Apr 2019].
- Ortea, E., Ríos, G., Benito, J. M., Pazos, C., and Coca, J., 2006. Treatment of oil-in-water emulsions: Performance of a sawdust bed filter ‘Angel filter’ filter ‘Angel. *Journal of Hazardous Materials*, 131, 195–199.
- OSPAR, 2000. Quality Status Report 2000 [online]. London. Available from: <http://www.ospar.org> [Accessed 4 Jan 2019].
- Pekala, R. W., 1989. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *Journal of Materials Science*, 24 (9), 3221–3227.
- Pettit, S. J. and Beresford, A. K. C., 2009. Port development: from gateways to logistics hubs. *Maritime Policy & Management*, 36 (3), 253–267.
- Port of Oulu, 2019. Port of Oulu - Port Handbook 2019 [online]. Oulu. Available from: http://www.e-julkaisu.fi/ouluport_handbook2019en/mobile.html#pid=30 [Accessed 11 Apr 2019].
- Port of Tromsø, 2019. Port of Tromsø Fishery port and service center [online]. Tromsø. Available from: www.tromso.havn.no [Accessed 11 Apr 2019].
- Potter, S., 2008. The use of consensus-based standards to improve oil spill equipment testing and selection protocols. *International Oil Spill Conference Proceedings*, 2008 (1), 427–429.
- Prince, R. C. and Clark, J. R., 2004. Chapter 18 Bioremediation of marine oil spills. *Studies in Surface Science and Catalysis*, 151, 495–512.
- Rotar, V. O., Iskrizhitskaya, D. V., Iskrizhitsky, A. A., and Oreshina, A. A., 2014. Cleanup of Water Surface from Oil Spills Using Natural Sorbent Materials. *Procedia Chemistry*, 10, 145–150.
- Ruiz, H. A., Ruzene, D. S., Silva, D. P., Da Silva, F. F. M. I., Vicente, A. A., and Teixeira, J. A., 2011. Development and characterization of an environmentally friendly process sequence (autohydrolysis and organosolv) for wheat straw delignification. *Applied Biochemistry and Biotechnology*, 164 (5), 629–641.

- Sabir, S., 2015. Approach of Cost-Effective Adsorbents for Oil Removal from Oily Water. *Critical Reviews in Environmental Science and Technology*, 45 (17), 1916–1945.
- SACs, 2001. Environmental impacts of oil sourced from ports and harbours [online]. Available from: http://www.ukmarinesac.org.uk/activities/ports/ph6_2_1.htm [Accessed 5 Apr 2019].
- Sai, H., Xing, L., Xiang, J., Cui, L., Jiao, J., Zhao, C., Li, Z., and Li, F., 2013. Flexible aerogels based on an interpenetrating network of bacterial cellulose and silica by a non-supercritical drying process †, 1–8.
- Sayed, S., Sayed, A. E., and Zayed, A., 2004. Oil spill pollution treatment by sorption on natural *Cynanchum acutum* L. plant. *Journal of Applied Sciences & Environmental Management*, 7 (2), 63–73.
- Scholz, D., Potter, S., Buist, I., Trudel, K., and Ross, -Sl, 2012. Spill Response in the Arctic Offshore [online]. Available from: https://www.api.org/~media/Files/EHS/Clean_Water/Oil_Spill_Prevention/Spill-Response-in-the-Arctic-Offshore.pdf [Accessed 17 Jan 2019].
- Šćiban, M., Klačnja, M., and Škrbić, B., 2006. Modified softwood sawdust as adsorbent of heavy metal ions from water. *Journal of Hazardous Materials*, 136 (2), 266–271.
- Sehaqui, H., Zhou, Q., Ikkala, O., and Berglund, L. A., 2011. Strong and tough cellulose nanopaper with high specific surface area and porosity. *Biomacromolecules*, 12 (10), 3638–3644.
- Siró, I. and Plackett, D., 2010. Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose*, 17 (3), 459–494.
- Sørstrøm, S. E., Brandvik, P. J., Buist, I., Daling, P., Dickins, D., Faksness, L.-G., Potter, S., Fritt-Rasmussen, J., and Singaas, I., 2010. Joint industry program on oil spill contingency for Arctic and ice-covered waters: Summary report [online]. Trondheim: SINTEF. Available from: [http://orbit.dtu.dk/en/publications/joint-industry-program-on-oil-spill-contingency-for-arctic-and-icecovered-waters\(7db212e9-52e2-4b5a-989b-efd4ad97351a\)/export.html](http://orbit.dtu.dk/en/publications/joint-industry-program-on-oil-spill-contingency-for-arctic-and-icecovered-waters(7db212e9-52e2-4b5a-989b-efd4ad97351a)/export.html) [Accessed 2 Apr 2019].
- Suchanek, T. H., 1993. Oil impacts on marine invertebrate populations and communities. *Integrative and Comparative Biology*, 33 (6), 510–523.
- Tan, C., Fung, B. M., Newman, J. K., and Vu, C., 2001. Organic aerogels with very high impact strength. *Advanced Materials*, 13 (9), 644–646.
- Teas, C., Kalligeros, S., Zanikos, F., Stoumas, S., Lois, E., and Anastopoulos, G., 2001. Investigation of the effectiveness of absorbent materials in oil spills clean up, 140, 259–264.
- Torgersen, T. and Huse, G., 2005. Variability in retention of *Calanus finmarchicus* in the Nordic Seas. *ICES Journal of Marine Science*, 62 (7), 1301–1309.

- USEPA, 2010. 11/12/2010: EPA Releases Reports on Dioxin Emitted During Deepwater Horizon BP Spill/Reports find levels of dioxins created during controlled burns were below levels of concern [online]. United State Environmental Protection Agency. Available from: https://archive.epa.gov/epapages/newsroom_archive/newsreleases/6a2165dcf5f0bb5f852577d9005acf94.html [Accessed 2 Jan 2019].
- Wahi, R., Chuah, L. A., Choong, T. S. Y., Ngaini, Z., and Nourouzi, M. M., 2013. Oil removal from aqueous state by natural fibrous sorbent: An overview. *Separation and Purification Technology*, 113, 51–63.
- Walday, M. and Kroglund, T., 2002. Biogeographical regions in Europe: the Arctic Ocean [online]. European Environment Agency. Available from: <http://edz.bib.uni-mannheim.de/daten/edz-bn/eua/02/BalticSea.pdf>.
- Wan, C., Lu, Y., Cao, J., Sun, Q., and Li, J., 2015. Preparation, Characterization and Oil Adsorption Properties of Cellulose Aerogels from Four Kinds of Plant Materials via a NaOH/PEG Aqueous Solution. *Fibers and Polymers*, 16 (2), 302–307.
- Wang, J., Zheng, Y., and Wang, A., 2013. Coated kapok fiber for removal of spilled oil. *Marine Pollution Bulletin*, 69 (1–2), 91–96.
- Wang, Y., Yadav, S., Heinlein, T., Konjik, V., Breitzke, H., Buntkowsky, G., Schneider, J. J., and Zhang, K., 2014. Ultra-light nanocomposite aerogels of bacterial cellulose and reduced graphene oxide for specific absorption and separation of organic liquids. *RSC Advances*, 4 (41), 21553.
- Wang, Z., Jin, P., Wang, M., Wu, G., Dong, C., and Wu, A., 2016. Biomass-Derived Porous Carbonaceous Aerogel as Sorbent for Oil-Spill Remediation. *ACS Applied Materials and Interfaces*, 8 (48), 32862–32868.
- Word, J. Q., 2014. Environmental Impacts of Arctic Oil Spills and Arctic Spill Response Technologies Literature [online]. Available from: http://neba.arcticresponsetechnology.org/assets/files/Environmental_Impacts_of_Arctic_Oil_Spills_report.pdf.
- Wu, D. and Fu, R., 2008. Requirements of organic gels for a successful ambient pressure drying preparation of carbon aerogels. *Journal of Porous Materials*, 15 (1), 29–34.
- Wu, D., Fu, R., Zhang, S., Dresselhaus, M. S., and Dresselhaus, G., 2004. Preparation of low-density carbon aerogels by ambient pressure drying. *Carbon*, 42 (10), 2033–2039.
- Wu, Z.-Y., Li, C., Liang, H.-W., Chen, J.-F., and Yu, S.-H., 2013. Innenrücktitelbild: Ultralight, Flexible, and Fire-Resistant Carbon Nanofiber Aerogels from Bacterial Cellulose (Angew. Chem. 10/2013). *Angewandte Chemie*, 125 (10), 3113–3113.
- Xiao, S., Gao, R., Lu, Y., Li, J., and Sun, Q., 2015. Fabrication and characterization of nanofibrillated cellulose and its aerogels from natural pine needles. *Carbohydrate Polymers*, 119, 202–209.
- Zanini, M., Lavoratti, A., Lazzari, L. K., Galiotto, D., Pagnocelli, M., Baldasso, C., and Zattera, A. J., 2017. Producing aerogels from silanized cellulose nanofiber suspension. *Cellulose*, 24 (2), 769–779.

- Zhang, Z., Sèbe, G., Rentsch, D., Zimmermann, T., and Tingaut, P., 2014. Ultralightweight and Flexible Silylated Nanocellulose Sponges for the Selective Removal of Oil from Water. *Chemistry of Materials*, 26 (8), 2659–2668.
- Zhang, Z., Tingaut, P., Rentsch, D., and Zimmermann, T., 2015. Controlled Silylation of Nanofibrillated Cellulose in Water: Reinforcement of a Model Polydimethylsiloxane Network, 2681–2690.
- Zhao, Y., Hu, C., Hu, Y., Cheng, H., Shi, G., and Qu, L., 2012. A versatile, ultralight, nitrogen-doped graphene framework. *Angewandte Chemie - International Edition*, 51 (45), 11371–11375.
- Zheng, Q., Cai, Z., and Gong, S., 2014. Green synthesis of polyvinyl alcohol (PVA)-cellulose nanofibril (CNF) hybrid aerogels and their use as superabsorbents. *Journal of Materials Chemistry A*, 2 (9), 3110–3118.
- Zhou, S., Liu, P., Wang, M., Zhao, H., Yang, J., and Xu, F., 2016. Sustainable, Reusable, and Superhydrophobic Aerogels from Microfibrillated Cellulose for Highly Effective Oil/Water Separation. *ACS Sustainable Chemistry & Engineering*, 4 (12), 6409–6416.
- Zhou, Z. Y., Tian, N., Li, J. T., Broadwell, I., and Sun, S. G., 2011. Nanomaterials of high surface energy with exceptional properties in catalysis and energy storage. *Chemical Society Reviews*, 40 (7), 4167–4185.
- Zou, J., Liu, X., Chai, W., Zhang, X., Li, B., Wang, Y., and Ma, Y., 2015. Sorption of oil from simulated seawater by fatty acid-modified pomelo peel. *Desalination and Water Treatment*, 56 (4), 939–946.

APPENDIX:

APPENDIX 1. GLOSSARY

Ballast water: The water carried in ship ballast tanks to improve the ships stability, trim and balance.

Biodegradability: The ability of organic substances to be broken down into simpler substances by enzymes from microorganisms.

Biodegradable: A substance that is capable of being decomposed by bacterial or living organisms.

Bioremediation: This is typically the use of microorganisms to breakdown environmental pollutants.

Brackish water: This is a water that saltier salt than fresh water but not as abundant as seawater.

Buoyancy: This is the tendency of a substance to float when they are submerged in a liquid.

Capillary effect: This is the ability of a liquid to rise through a tube.

Cross-linking: This is the bonding of one polymer chain to another polymer chain.

Crystalline: A solid substance or material having the structure of a crystal.

Electrostatic interaction: They are also called van der Waals interaction. The attractive interaction between objects that have electric charges.

Emission: A release of a substance into the air. They can be harmful or not harmful.

Explosive limit: The maximum concentration of a gas, which will burn in the air.

Fermentation: This is the anaerobic breakdown of compounds by enzymes

Fiord zone: This is a narrow inlet of a sea, which is bordered by steep cliffs.

Flammability limit: This is the upper and lower limits of a vaporised fuel at a fixed temperature and pressure, which can cause an explosion.

Flammable liquids: They are liquids with flash point at 37.8°C or lower than 93.3°C.

Gelation: The action of the process of freezing

Hazardous cargo: They are known as dangerous goods or hazardous goods.

Hydrocarbons: They are compound that consist of carbon and hydrogen.

Hydrophobicity: This is the physical property of a molecule, which is obviously fend off from a mass of water.

Hydrophobic materials: They are materials or surfaces, which resists water, and they are usually nonpolar materials. The atoms within the substance or molecule do not produce a static electric field.

Ice cover: This is the ice that cover the sea area or surface.

Marine environment: An environment that care for marine life, e.g. sea, ocean etc.

Maritime traffic: It shows the real time vessels information, location of ships and sea movements through sea.

Mechanical strength: This include the yield strength, tensile strength and fatigue strength of a substance. The material able to resist cracks and deformation.

Melting point: This is the temperature at which a substance changes from solid to liquid.

Mineralization: This is a biological process in which organic materials are concerted to inorganic substances by microorganisms with the soil.

Molecular weight: The mass of a molecule or a substance.

Morphology: This is the study of shapes and the structural arrangement of substance.

Neutral reaction: This is when a strong acid and a strong base reacts in a solution and a pH of 7 is obtained.

Oil retention: This is the ability of a material to retaining oil.

Partition coefficient: This refers to the concentrations of two immiscible liquids at an equilibrium.

Pollutant: A substance that causes pollution, e.g. oil

Pollution: This is the introduction by man, directly and indirectly of substances into maritime areas, which result in hazard to cause health, harm living organisms and marine ecosystem.

Polymerization: This is the chemical reaction at which two or more molecules come together to form large ones that will have the same structure.

Porosity: This is the measure of the void spaces in a material.

Porous substance: This is a material that contains pores or voids.

Pyrolyzing: Decomposition through heating to a high temperature.

Reaction rate: The speed at which reactants are converted into products or the concentration change per unit time.

Recyclability: The ability of a waste material to be able to be captured and converted into new item.

Ribbon-like shape: A shape in a form of a ribbon.

Salinity: The measure of the dissolved amount of salt in seawater.

Semi-crystalline polymer: They are polymers that have high ordered molecular structure with a fast melting point. These materials have excellent chemical resistance.

Solubility: Solubility is a chemical property, which measures the ability of a solute to dissolve in a solvent. The resulting solution is called known as saturation. Solubility of oil measures the amount of oil that dissolves in water. The more polar the compound the more soluble it becomes in water. Polarity of a compound is the separation of electric charge that leads to a molecule. The chemical groups in the compound have an electric dipole moment, with negative charge at one end and positive charge at one end. The solubility of oil in water is low and is an important factor to consider after oil spill accidents.

Surface tension: This is the force of attraction that is exerted upon the surface of a molecule.

Temperate climate condition: A climate condition without extremes of temperature and precipitation.

Topographically: This relate to the word topography.i.e. the physical appearance of natural features of land or sea area

Ultralight: Extremely light in mass and weight.

Van der Waal forces: The force of attraction or intermolecular forces that exist between molecules.

Viscosity: The state of being thick or sticky. The viscosity of oil is the resistance of the oil to flow.

Water column: This is the vertical section of water that extends from the sea surface to the bottom of the sea.